

Colloidal stability of surfactant-free radiation curable polyurethane dispersions

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Received 15 June 2005; received in revised form 12 August 2005; accepted 15 August 2005

Abstract

Radiation-curable polyurethane dispersions (UV-PUDs) are colloidal dispersions whose stability is mainly ensured by the electrostatic repulsion between the negatively charged polymer particles. In this article, particle stabilization is presented in terms of the physico-chemical characteristics of the polymer dispersion and its microstructure. The phenomenon of the colloidal destabilization at higher temperature is studied by multiple light scattering, then correlated with the evolution of the particle size distributions and the measurement of the apparent critical coagulation concentration of a salt as an indication of the energy barrier at the surface of the particles. The investigation of selected chemical parameters of the polymer on the colloidal stability aims to identify the most relevant ones with an understanding of the underlying mechanism. The study underlines that UV-PUDs constitute a waterborne polymer family with its own identity, adding complexity to the traditional radiation curing chemistry. Finally, it highlights the new perspectives offered for novel environmental-friendly products with high-end performance and extended stability and robustness.

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Keywords: UV-PUD; Polyurethane dispersion; Radiation-curing; Colloidal stability; Environmental-friendly

1. Introduction

The whole family of waterborne polymers is gradually dominating the surface coating market as a consequence of a lower chemical impact on the environment and a continuously improving level of performance.

Polyurethane dispersions (PUD) and especially radiation-curable polyurethane dispersions (UV-PUD) [1–3] have benefited over the last few years from a growing attention by the market recognizing their high-end performance and strong potential [4]. These are aqueous dispersions of acrylated polyurethane oligomers that are thus positioned at the interface between various technologies [5]. They provide coatings with strong performance and unique functionality taking advantage *at the same time* from: (i) colloidal dispersions; (ii) radiation curing and (iii) polyurethane polymers. We discuss these three main features in the perspective of innovative surface specialties providing high-end performance for wood and plastics [6]; although metal,

concrete, glass, textile, or graphic art applications have also been considered so far.

1.1. Radiation curable polyurethane polymers

UV-PUDs are true polyurethane oligomers. The hard urethane or urea domains with strong hydrogen bonding, together with the acrylate cross-linking reaction, give the structure its hardness and resistance – while the softer domains serve as buffer zones and account for the flexibility and impact resistance. A superior balance in chemical resistance and mechanical properties – like (cold) flexibility and impact deformation – is obtained when compared to 100% UV systems, due to the lower cross-linking density and the higher average molecular weight between cross-links. The influence of the cross-linking density and the molecular weight between cross-linking knots on the coating performance was reported elsewhere in the case of 100% systems [7] and UV-PUDs [8]. In many cases, the cured coating offers an ultimate mechanical and chemical resistance to the surface, associated within a set of performance specific to the substrate and the application – like an improved adhesion. The instant and low-energy radiation

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curing offers an additional benefit over the usual thermal cure.

1.2. Colloidal dispersions

UV-PUDs are colloidal dispersions whose stability is generally ensured by the electrostatic repulsion between the anionic surfaces of said polymer particles.

Their waterborne nature militates in favor of high environmental, health and safety standards (low VOC). They are completely miscible with water and they offer also broad formulation options – like the possibility to target coatings with a large window of gloss.

The complex heterogeneous nature of these dispersion implies that their rheology becomes essentially independent of the molecular weight of the polymer, and is now mainly determined by a complex relationship between: (i) the particle volume fraction (solid content); (ii) the particle size distribution and morphology; (iii) the particle interactions and (iv) the composition of the aqueous phase. UV-PUDs are consequently very low viscous products with a favorable rheology for applications such as spray or flexography/heliogravure.

The minimum film formation temperature (MFFT) of these low molecular weight oligomers dispersed in water is below room temperature and does not require the use of coalescing agents. The layer formed after particle coalescence is generally tack-free before cure (decreases dust contamination and heat blocking) and sometimes water-soluble before cure (reduces the premature drying of the polymer under coating application). In any case, the material becomes very hard and resistant after curing.

In order to compete for the many advantages that these polyurethane dispersions can offer when compared to their 100% counterparts, they have also to minimize the eventual drawbacks associated with their status of colloidal dispersions. In this perspective, the colloidal stability of the product is particularly important since the UV-PUD dispersion is supposed to maintain its physico-chemical integrity over the time in a wide range of thermal, mechanical or chemical stresses with no change of aspect or destabilization occurring.

Extreme temperatures, although prohibited, are frequently observed during the transport and may render the product further unusable following its destabilization. It is possible to determine the average time required to destabilize any product as a function of the temperature. A temperature of 60 °C was found to be ideal to study the stability in a suitable time frame for the experimentalist as well as being connected with the extreme temperatures sometimes recorded during the life cycle of a product. Doing so, it is possible to record a wide range of heat stability requesting a serious investigation of the physico-chemical parameters able to guarantee the suitable long-term robustness. We will consider a stable product if the stability is equal or superior to 10 days at 60 °C. The best products will reach more than 60 days under these challenging conditions prior to their destabilization in the form of a solid aggregate visually observed at the bottom of the test bottle.

The objective of this study was two-fold: (i) first, to develop the right methodology in order to study and compare the colloidal stability at room or at elevated temperatures; (ii) secondly, to determine and understand the physico-chemical parameters involved in order to optimize the stability of new UV-PUDs.

2. Description of the colloidal stability

2.1. Generalities

In its broadest definition, colloidal dispersions refer to sub-micron particles typically within a size range of 1–1000 nm. The formation of colloidal particles from the bulk material is accompanied by a change in the standard-free energy of the system, ΔG_f° . This is represented in Fig. 1 in which the $\Delta G_f^\circ = \gamma_{sl}\Delta A_{sl}$ can be either negative or positive. In this equation, γ_{sl} is the solid–liquid interfacial surface tension or free energy and ΔA_{sl} is the increase in interfacial area. If ΔG_f° is negative, the colloid is thermodynamically stable (lyophilic) but if ΔG_f° is positive, the colloidal state is unstable relative to the bulk (lyophobic).

The lyophobic colloids, even if they are thermodynamically unstable, can be made *metastable* for a long period of time if an energy barrier (E_{act}) of a sufficient height opposes the colloidal state to the bulk state. When the barrier is absent or too small, then the particles tend to recover the bulk state by aggregating in a reversible or an irreversible way. This process is known as the *flocculation* (reversible) or *coagulation* (irreversible). The natural tendency of colloidal particles to aggregate is coming both from the thermal energy of the particles – also known as Brownian motion – and the dipole–dipole attractions among uncharged molecules – usually described as the van der Waals interaction.

The frequency and efficiency of the inter-particle collisions depend on the number and size of the particles in the dispersion. For a model dispersion of uniform spherical particles, Fig. 2 shows that the ratio between the inter-particle distance (H is the distance between the particle surfaces) and the particle diameter, i.e., $2a$ where a is the radius, drops below unity at volume fractions >10%, i.e., here the inter-particle distance becomes a fraction of the particle diameter. This is even more the case at the typical solid contents of the UV-PUD systems, e.g., 35%, where the

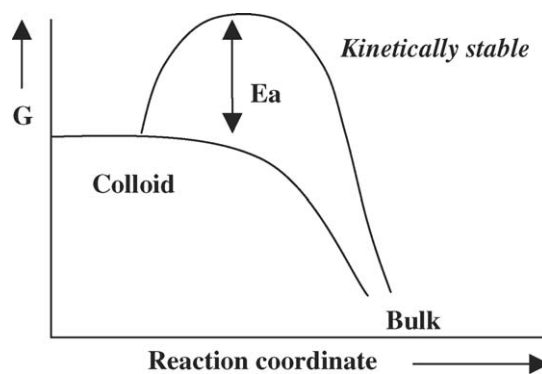


Fig. 1. Representation of the free energy change between bulk and colloidal states in a lyophobic colloidal dispersion; the activation energy (E_{act}) accounts for a kinetically stable system.

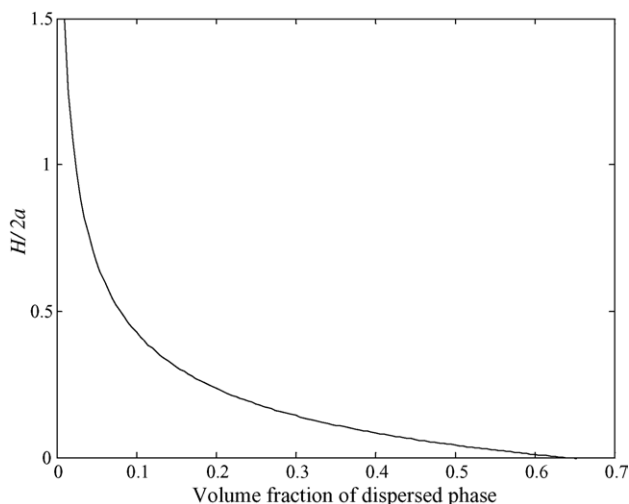


Fig. 2. Ratio of the sphere separation distance and the particle diameter as a function of particle volume fraction for a dispersion of uniform spherical particles in random packing.

inter-particle distance drops to less than one-fifth of its diameter. This simplified picture emphasizes the challenge of reaching a good stability in such thermally agitated close-packed systems.

Fig. 3 stresses the extremely high specific surface areas developed in the colloidal state for spherical particles within the range 10–1000 nm. In the case of particles of 100 nm and lower (which is generally the case in the practice), the surface developed by the particles is reaching 100 m²/g and more. This is a phenomenal surface developed by particles in close contact and illustrates the level of interactions between them.

The pathways leading to irreversible dispersion breakdown are typically preceded by flocculation and involve coagulation, gravitational separation by creaming or sedimentation, gelification and coalescence. Ostwald ripening happens in specific conditions.

2.2. Classical colloidal stability theory

According to the nature of the polyurethane dispersions studied in this work, the primary mechanism of colloid stability is

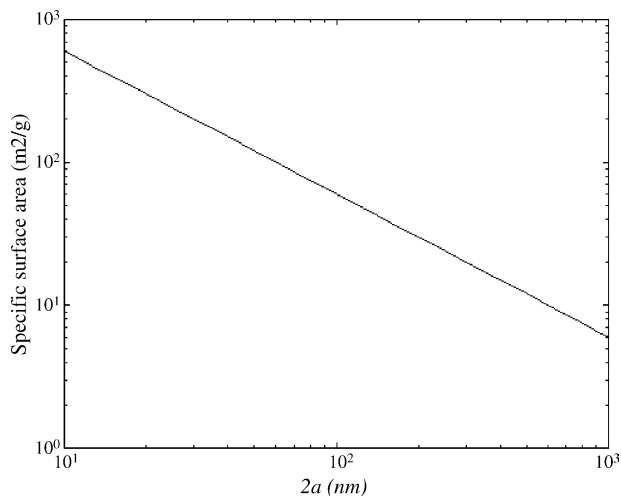


Fig. 3. Specific surface area vs. particle diameter for uniform spherical particles.

electrostatic repulsion of the electrically charged polymer particles [9]. Dependent on the polymer backbone composition, particles with a substantial hydrophilic character can be produced. As a consequence, water swelling may actually result in microgel particles [9–11]. The degree of swelling is additionally affected by factors such as particle charge (viz. pH), molecular weight, electrolyte content, temperature, etc. [11]. This potential effect should be considered in the elucidation of the stability behavior of the polyurethane dispersion but, however, was ignored in a first approximation.

In the assumption of negligible steric repulsion, the particle pair interaction potential is essentially described in terms of the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory where the electrical double layer (EDL) repulsion is expressed as [12–14],

$$V_R = \frac{32\pi\epsilon\epsilon_0(k_B T)^2 a}{z^2 e^2} \tanh^2 \left(\frac{ze\psi}{4k_B T} \right) \exp(-\kappa H) \quad (1)$$

and the van der Waals attraction reads as,

$$V_A = -\frac{A}{6} \left(\frac{2a^2}{H(4a+H)} + \frac{2a^2}{(2a+H)^2} + \ln \left(\frac{H(4a+H)}{(2a+H)^2} \right) \right) \quad (2)$$

where a is the particle radius, H is the distance between the particle surfaces, A is the Hamaker constant, ψ is the surface (Stern) potential, z is the electrolyte valence, T is the absolute temperature and $1/\kappa$ is the Debye length. The other constants are defined as usual, i.e., k_B is Boltzmann's constant, e is the elementary charge, ϵ the relative dielectric constant of the solvent and ϵ_0 the permittivity of vacuum. The Hamaker constant embraces all characteristics of the particle material that might affect the attraction.

The EDL is formed by surface-bound ionic groups and an equal number of opposite charge in the vicinity of the particle surface, which forms a mobile diffuse layer. The thickness of the diffuse part of the EDL is characterized by the inverse Debye length expressed as

$$\kappa = \left(\frac{2e^2 N_A I}{\epsilon\epsilon_0 k_B T} \right)^{1/2} \quad (3)$$

where I represents the ionic strength of the aqueous medium and N_A is Avogadro's number.

It is noticed that the surface potential ψ cannot be measured directly but the zeta potential, corresponding to the junction (slip plane) between the stern layer of ions rigidly attached to the colloid and the diffuse layer of counter-ions moving around the particle, can be determined experimentally from electrokinetic measurements [12]. The zeta potential is related to the mobility of the particle in an electric field.

For $H/2a \ll 1$, the attractive energy, Eq. (2), reduces to

$$V_A = -\frac{Aa}{12H} \quad (4)$$

and provides a fair approximation for the attraction energy in general [14]. The total pair-potential V_{tot} is the sum of the two

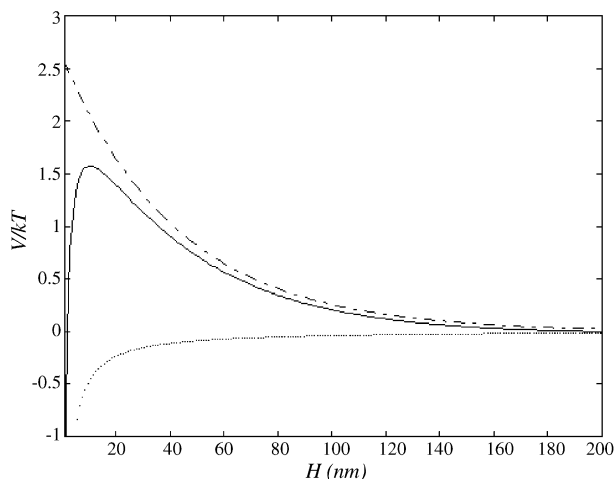


Fig. 4. DLVO interaction potential V_{tot} vs. sphere separation distance (full line). The dotted line represents the repulsion potential V_R whereas the dashed line shows the attraction potential V_A (as detailed in the text).

contributions,

$$V_{\text{tot}} = V_R + V_A \quad (5)$$

In Fig. 4, the total DLVO potential V_{tot} was calculated as a function of the sphere separation distance H using parameter values representative for the investigated UV-PUDs (vide infra) at 25 °C, i.e., $a = 50$ nm, $\psi = 10$ mV, $A = 10^{-20}$ J and $I = 50$ mM. The interaction energy presents a maximum ($\approx 1.5 k_B T$) at a certain distance. For a sufficiently high-energy barrier, the system will remain stable as the particles cannot overcome the barrier through thermal agitation. Increasing the concentration of electrolyte will compress the EDL and reduce the electrostatic repulsion between the particles. The electrolyte concentration at which the energy barrier vanishes is known as the critical coagulation concentration (ccc).

2.3. Physico-chemical parameters

There are many physico-chemical parameters that influence the colloidal stability of the polymer dispersion. Several of them can be fine-tuned by playing on the chemical design of the polymer.

The polymer nature plays an essential role and determines primarily the surface charge density. This includes (i) the nature of the polymer backbone – diisocyanates and diols, (ii) the nature and amount of the acrylated capping agent and (iii) last but not the least, the nature and amount of the build-in ionic chemical groups and counter-ions. Frequently, the dimethylol propionic acid is incorporated into the oligomer as a diol and brings a carboxylic acid functionality easily neutralized in carboxylate salts. It is worth mentioning that an excess of ionic functionality, although beneficial for the electrostatic repulsion between particles, will be detrimental in other performance areas linked to an excess of water and solvent sensitivity and an increased sensitivity to premature hydrolysis. Any other remaining organic function on the polymer can have a remarkable impact on the colloidal stability.

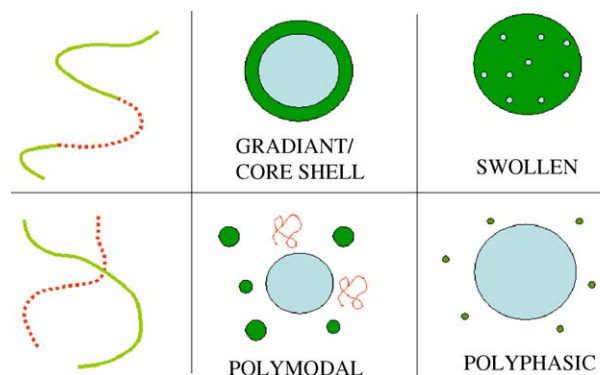


Fig. 5. Schematic representation of the polymer microstructure and the particle morphology.

The dispersion process is known to have a fine-tuning influence on the dispersion characteristics; the shear employed for making the dispersion combined with the several possible types of neutralization and dispersion process can retain the attention. It is worth to mention that the particle sizes, although not affecting directly the surface charge density, should be low enough (ideally, this means around or below 100 nm) to provide stable colloids.

An ideal colloidal system is considered as a uniform monomodal dispersion of a chemically homogenous polymer. However, many uncontrolled parameters are causing deviations from this ideal picture and affect the particle size distribution and the microstructure of the dispersion. Some typical possibilities are outlined in Fig. 5 and underline an infinite complexity. First, the particle can display heterogeneity of composition when going from the center to the outside of the particle: a typical morphology is then “gradient” or “core–shell” [15] but even more complicated structures are known. Secondly, the dispersion can display inter-particle heterogeneity of composition, size and shape: particle size distributions can be multi-modal and the chemical composition between the populations can vary to a large extent, either as a result of the process used or as a result of the chemist’s actions. In the case of polymer particles “swollen” either with water or with a co-reactant or a co-solvent, the rules of colloidal stability are also likely to be changed. The same can be observed with poly-phasic systems where a major polymer dispersion cohabits with a minor emulsion population.

The composition of the water phase is relevant if it contains water-soluble oligomers providing a tensio-active effect. Similarly, any insoluble material from the reaction medium present in the form of additional droplet emulsions can also affect the colloidal stability. The nature of the counter-ions as well as the degree of neutralization (essentially linked to the pH of the aqueous phase in the case of weak bases like carboxylate salts) and the overall ionic strength also plays a determining role in the colloidal stability.

3. Experimental

3.1. Preparation of polyurethane dispersions

The chemistry of the UV-PUDs is outlined in Fig. 6. In a first step, a low molecular weight polyurethane prepolymer

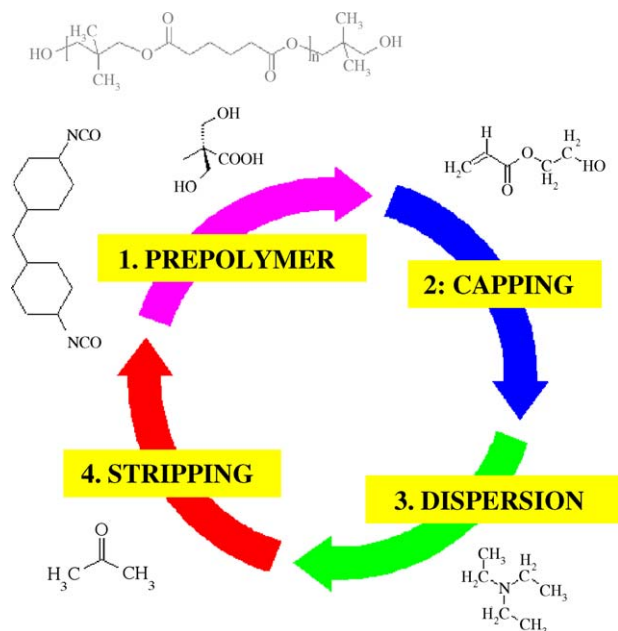


Fig. 6. Representation of the four chemical steps involving the synthesis of unsaturated polyurethane dispersions.

is synthesized in a low boiling point solvent (like acetone) both from a diisocyanate (represented in Fig. 6 by methane-dicyclohexyl-diisocyanate, H12MDI) and from long and short chain diols. Long-chain diols are selected from polyester, polyether or polycarbonate and are used to provide the flexible segments of the polymer (represented in Fig. 6 by a neopentylglycol polyadipate). Short-chain diols (functional or not) are used to impart stiffness and/or to provide the ionic moieties required for water dispersion (represented in Fig. 6 by dimethylolpropionic acid, DMPA). In a second step, the carboxylated, isocyanate-terminated polyurethane prepolymer is capped with a hydroxylated acrylate molecule (represented here by hydroxyethyl acrylate, HEA). During a third step, the pre-polymer is dispersed into water under high shear mixing after neutralization of the carboxylic acid functions with a tertiary amine (e.g., triethylamine). In a fourth step, the low boiling point solvent is stripped out under vacuum. The resulting UV-PUDs exhibit generally a solid content between 35% and 45%, a pH value between 7 and 8 and an average particle size below 100 nm.

3.2. Characterization of polyurethane dispersions

The solid content of the dispersions was determined gravimetrically by drying an aliquot of the stock dispersions for 2 h in a heat convection oven at 120 °C. The viscosity was measured with a Brookfield viscometer at a shear rate of 50 rpm and 25 °C. The hydrodynamic particle diameter, d_{DLS} , of the dispersed particles was determined by dynamic light scattering (DLS). The experiments were performed at room temperature using a Malvern Autosizer LoC instrument linked to a Malvern Series 7032 Multi-8 correlator. The laser wavelength is 670 nm and the observation angle for the scattered light was 90°. Samples were prepared in 4 ml PMMA cells and distilled deionized

(DI) water (MilliQ, resistivity 18 MΩ cm) was used for sample dilution.

3.3. Colloidal stability and critical coagulation concentration (ccc)

In this preliminary work, the colloid stability of the neat UV-PUD dispersions was first evaluated at 60 °C using a phenomenological approach. Next, we used a physico-chemical approach in order to assess the energy barrier of the particles in dilute conditions through the modification of the ionic strength of the medium.

3.4. Qualitative assessment of colloidal stability by multiple light scattering (MLS)

The aging of the dispersions at 60 °C was followed by multiple light scattering (MLS). The MLS experiments were carried out using a Turbiscan Lab™ Thermo (temperature controlled) equipment from Formulacion [16]. A pulsed near infrared light source (880 nm) scans the sample from bottom to top and two synchronous detectors acquire: (a) the light intensity transmitted through the sample (T = transmission) and (b) the light scattered at an angle of 120° (B = backscattering), both expressed relative to the incoming light intensity. Samples are prepared in flat-bottomed optical quality glass tubes with 27.5 mm diameter and 70 mm height. The transmitted light evidences the clarification in the sample (increasing T). The backscattered signal responds to both particle concentration and particle size evolutions in the sample. The advantage of MLS is that it handles neat dispersions without further dilution or modification. At a constant volume fraction, the back scattering signal behaves as a bell-shaped curve as a function of particle size with a maximum around the source laser wavelength (i.e., 880 nm). At a constant particle size, the back scattering signal is proportional to the logarithm of the volume fraction. Similarly, the transmission increases upon decrease of the volume fraction of the dispersion at a constant particle size. Consequently the simultaneous monitoring of transmission and back scattering of a colloidal dispersion during aging (along the whole sample) is a rich source of information since it responds to both particle size increase (floculation) and particle migration (sedimentation or creaming). The two phenomena may appear simultaneously or consecutively.

3.5. Qualitative assessment of colloidal stability by dynamic light scattering (DLS)

In parallel to the MLS experiments, the ageing of the dispersions at 60 °C was followed by dynamic light scattering (DLS) using a Malvern Autosizer Lo-C single angle measurement. The DLS experiments were carried out after taking aliquots of the aged dispersion at a fixed height inside the sample tube. This method proves to be very valuable when applied in parallel with MLS. It is able to evidence the appearance of floculation of the sample far better than by visual inspection.

Table 1
Characteristics of the polyurethane dispersions

Model	Capping type	Capping (%)	Neutralization type	Solid content (%)	pH	Particle size (nm)	COOH (mmol/g)	t_{\max} (h)	ccc (mmol/L)
A1	A	60	TEA	35	7.8	31	0.59	~1200	~300
B1	B	60	TEA	35	7.8	57	0.43	~400	~300
B2	B	HMDA ^a	TEA	35	8.0	24	0.42	~300	~100
B3	B	60	NaOH	35	7.0	59	0.43	~500	~250
B5	B + D ^b	60	TEA	40	7.7	96	0.39	~350	~200
C1	C	60	TEA	35	7.8	43	0.45	~1400	~300
C2	C	100	TEA	35	7.7	43	0.38	~1070	~120

^a Chain extension with hexamethylene diamine.

^b Non-reactive poly-acrylate molecule.

3.6. Determination of the apparent ccc by dynamic light scattering (DLS)

A sample of the stock dispersion was diluted down to ~5 wt.% solids using distilled deionized water. Next, 10 ml of the diluted dispersion was added in an agitated test tube containing 1 ml NaCl solution. The concentration of the NaCl solutions was adjusted in order to cover a concentration range of 0–650 mmol/L in the diluted dispersion. Beyond the ccc, coagulation was observed almost instantaneously as expected. Below the ccc, the hydrodynamic particle size of the samples could be determined by DLS (signal acquisition time of 3 min) immediately after preparation.

4. Results and discussion

4.1. Synthesis of polyurethane dispersions

A model UV-PUD was prepared along the methodology described before in this article. It starts from the synthesis of an isocyanate-terminated polyurethane pre-polymer build from methane-dicyclohexyl-diisocyanate (H12MDI), a low molecular weight polyadipate of neopentylglycol (PANPG) and dimethylolpropionic acid (DMPA).

Several variations were introduced to this basic recipe and are outlined in Table 1.

Firstly, the nature and the stoichiometry of the capping agent varied. The first synthesis used a pure aliphatic alcohol (namely butanol) as capping agent and is referred to as type A. The absence of any reactive acrylic unsaturation makes it a reliable model to study the colloidal stability. For the other model synthesis, (poly)acrylated aliphatic alcohols, such as hydroxyethylacrylate (HEA) or pentaerythritol-triacrylate (PETIA), shown in Fig. 7, were used. They are referred to as types B, C and D. It is worth to mention that the chemical composition of higher acrylates is a complex homologous mixture of products deriving from the acrylation reaction; this has been studied recently in [17]. Some of them will bear at least one hydroxyl functionality capable to react with the terminating isocyanate of the pre-polymer. In contrast, the acrylated species without hydroxyl functions will not be covalently linked to the isocyanate-terminated pre-polymer and will remain as free molecules distributed between the aqueous and the polymer

phase. It is likely that these molecules play a role in the stability of the final dispersions. Except one, all the syntheses were made with a partial capping of the available isocyanate in the pre-polymer, i.e., not all the available isocyanate functions are reacted.

Secondly, the nature of the chain extension was considered. The controlled reaction of the remaining isocyanates with a diamine, and the subsequent modification of the chemical structure, is a relevant parameter. The remaining isocyanates were chain-extended with a diamine (i.e., hexamethylene diamine, HMDA) just after the dispersion of the pre-polymer in water.

Finally, the nature of the neutralizing agent and the resulting counter-ion was of a major interest in this study. For this reason, the triethylamine (TEA) was replaced with sodium hydroxide (NaOH) in one of the dispersions. In this case, the sodium hydroxide was dissolved in water prior to the dispersion of the pre-polymer.

The characteristics of the neat dispersions are summarized in Table 1. The seven one-parameter-at-the-time syntheses target the same dry contents (except B5) and the same pH. The resulting particle size distribution is the result of the chemistry and process, but generally falls well below 100 nm and is thus comparable. It is considered that the particle size variation among the dispersions is not predominant over the chemical modifications.

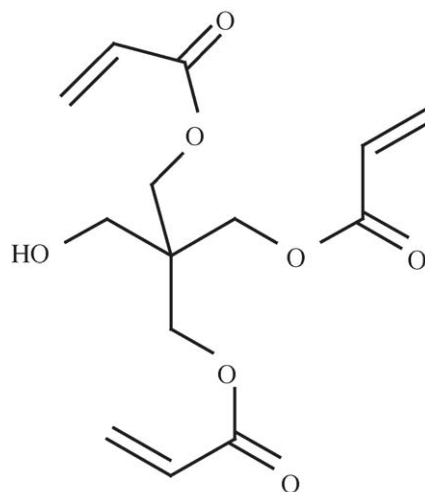


Fig. 7. Illustration of an idealized chemical structure of the pentaerythritol triacrylate (PETIA) used for the synthesis of a model colloidal dispersion.

4.2. Aging at 60 °C

All the prepared dispersions exhibit extended storage stability at 25 °C. In order to verify the storage stability in critical conditions, the dispersions were stored at 60 °C and periodically analyzed by MLS. In general, all the dispersions exhibit the same destabilization pathway as observed from the evolution of the transmission and the backscattering signal by MLS.

First, there is a uniform decrease of the transmission and increase of the back scattering over the whole sample; this is attributed to an increase in particle size through aggregation. Second, there is a wave appearing in the back scattering at the bottom of the sample due to the migration of the particles. Third, there is another wave in the back scattering on top of the sample resulting in the clarification of the dispersion. Forth, the deposit is growing and reaches its maximum height. Fifth, the deposit becomes clear meaning that the particles coalesce in a condensed phase – which is visible through the increase of transmission and the decrease of back scattering. Sixth, the enhancement of the light transmission through the aqueous phase corresponds to the end of the clarification. Fig. 8 displays the evolution of the backscattered signal with storage time at a height of 20 mm, corresponding to mid-height in the sample. All the curves show a maximum at ageing times, which varies significantly for the different dispersions. The increase in BS reflects an increase in particle size due to coagulation and/or coalescence whereas the subsequent decrease in BS combines particle size growth (BS starts to decrease beyond 880 nm particle size) and decrease of particle concentration due to sedimentation as also inferred from the enhanced light transmission. The location in time of the maximum, t_{\max} , can be used to rank the dispersions with respect to their colloidal stability. In Table 1, a coarse ranking of the dispersions can be established with increasing stability (t_{\max}).

Fig. 9 shows the evolution of the average hydrodynamic particle size upon ageing time for samples stored at 60 °C. The results are in agreement with the MLS data as the most unstable systems exhibit an average particle size increasing to very high values (above 300 nm) with ageing (flocculation). Alternatively, the most stable dispersions keep a low average particle size (≈ 100 nm).

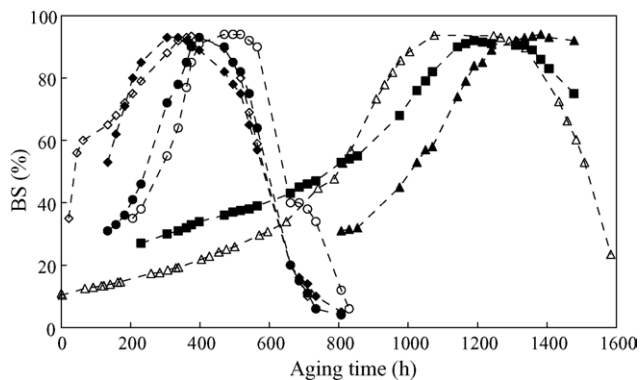


Fig. 8. Backscattering signal vs. aging time at 60 °C. Symbols: B1, filled circles; B3, open circles; B2, filled diamonds; B5, open diamonds; A1, squares; C1, filled triangles and C2, open triangles.

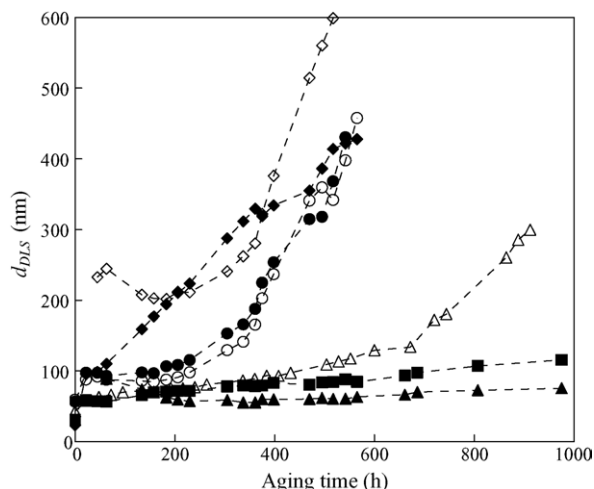


Fig. 9. Time-evolution of the hydrodynamic particle size obtained by DLS of representative samples aged at 60 °C. Symbols: B1, filled circles; B3, open circles; B2, filled diamonds; B5, open diamonds; A1, squares; C1, filled triangles and C2, open triangles.

4.3. Apparent critical coagulation concentration

Fig. 10 shows the dependence of the hydrodynamic particle size as a function of added NaCl concentration. The limiting concentration before rapid coagulation of the dispersion is used as an indicative value for the ccc. However, other electrolytes resulting from the dispersion preparation were not taken into account for their contribution to the ionic strength of the aqueous medium. Table 1 provides an overview of the *apparent* ccc for the investigated PUDs.

A higher ccc value is often associated to a higher electrostatic potential resulting in a better stabilization mechanism. An expression for the ccc can be derived assuming that the transition between stability and coagulation occurs for the condition of $V_{\text{tot}} = 0$ and $dV_{\text{tot}}/dH = 0$. According to the previous assumptions

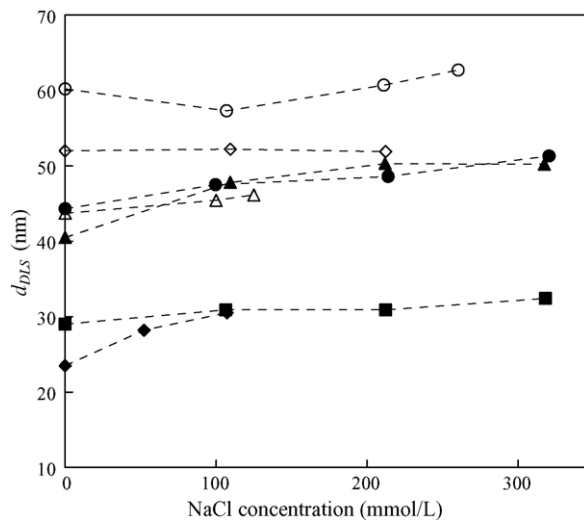


Fig. 10. Dependence of hydrodynamic particle diameter as a function of NaCl concentration. Symbols: B1, filled circles; B3, open circles; B2, filled diamonds; B5, open diamonds; A1, squares; C1, triangles and C, open triangles.

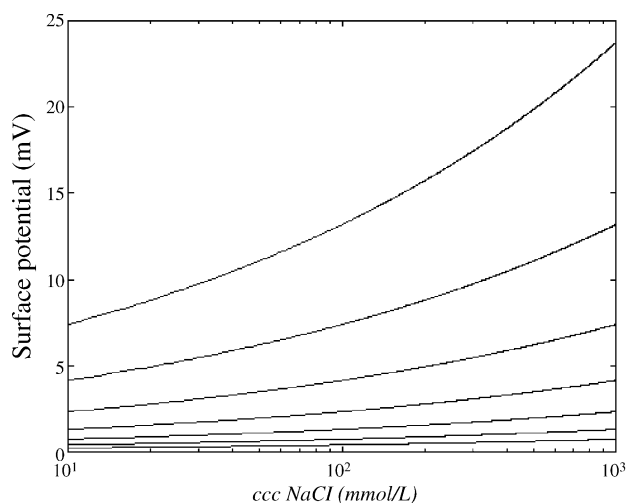


Fig. 11. Surface (Stern) potential vs. ccc of a monovalent electrolyte as calculated from Eq. (5) with $A = 10^{-22}, 10^{-21.5}, 10^{-21}, 10^{-20.5}, 10^{-20}, 10^{-19.5}$ and 10^{-19} J (curves shift upwards with increasing Hamaker constant).

for the interaction potential, the following relation is obtained,

$$\text{ccc} = \frac{9.85 \times 10^4 \varepsilon^3 \varepsilon_0^3 k_B^5 T^5}{N_A e^6 A^2 z^6} \tanh^4 \left(\frac{ze\psi}{4k_B T} \right) \quad (6)$$

From Eq. (6), the surface potential ψ can be further evaluated if values for the parameters are available. Aside from the crude ccc estimations, no values could be suggested for the dielectric constant ε of the aqueous medium and the effective Hamaker constant A for two polyurethane particles interacting across this medium. Nonetheless, as a guideline, ψ (at 25 °C) was calculated using the dielectric constant of water, i.e., $\varepsilon = 78$ within a range of Hamaker constants typical for aqueous dispersions, i.e., $10^{-22} \leq A \leq 10^{-19}$ J. The computed values of ψ are plotted as a function of ccc in Fig. 11 where the curves shift upwards for increasing A value. From this plot, it appears clearly that a single determination of ccc does not allow to determine the balance between electrostatic repulsion and van der Waals attraction. Independent values of A or ψ are required in order to draw further conclusions.

Fig. 11 also indicates that for the determined range of ccc (between 100 and 300 mM) the surface potential is relatively low, i.e., ≈ 10 –20 mV ($< k_B T/e = 25.7$ mV at 25 °C) at the highest A -value considered in this plot. The foregoing may suggest that the dispersions are critical with respect to stability but the value of the predictions is strongly limited by the crude assumptions, and in particular the rough ccc estimations. In addition, it is noticed that for the sake of simplicity steric effects and swelling aspects were omitted in the discussion and should be investigated in more detail.

It is possible to calculate theoretically the total concentration of ionisable carboxylic acid groups from the polymer composition (in mmol/g of polymer). The results are given in Table 1. It can be inferred that the expected variation in carboxylic concentration accounts only partially for the difference in colloidal stability. For instance sample A1, one of the most stable dispersions, possess the highest acid content; whereas samples B1, C1 and B5 which span a large stability range, were prepared using

nearly the same carboxylic acid concentrations. This clearly points out the complexity of the systems and the contribution of parameters other than the straightforward ionic charge of the particle, like the composition of the water phase.

4.4. Mechanical stability

All the dispersions considered in this study present an excellent mechanical stability up to very high shear rates ($10,000 \text{ s}^{-1}$). The mechanical stress is clearly not a critical parameter to destabilize our model dispersions and is thus not found to be relevant for this study. The good level of colloidal stability of these products makes them suitable for high-shear application experienced with spraying and roll coating.

5. Conclusions

The radiation curable polyurethane dispersions are not thermodynamically stable colloidal systems, although they are kinetically stable over challenging conditions of thermal, chemical and mechanical stress which make them robust enough to accept extreme conditions of handling, transport and storage. The limitations recorded for the stability of those dispersions are inherent to the technology used.

The phenomenology of the colloidal destabilization can be studied at elevated temperature (60 °C) on the original concentrated dispersion using an approach based on multiple or dynamic light scattering. It involves six distinctive steps, where a first increase of the particle size through flocculation and coagulation is responsible for the subsequent particle sedimentation and the clarification of the sample.

The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory accounts for the essentially ionic nature of the colloidal stabilization and permits the calculation of particle surface potentials from the determination of the critical coagulation concentration (ccc) of salts. These results are correlated with the theoretical concentration of ionic functions calculated from the polymer composition and can explain some of the results. They are also in fair agreement with the results from light scattering at 60 °C. The determination of the ccc presents a benefit as a rapid evaluation tool of the colloidal stability and can be proposed as a control test for the development of new equivalent products with excellent stability.

The chemical variants reveal that – beyond the chemical nature of the polyurethane backbone and the ionic component – the nature and the amount of the acrylated capping agent are essential to the colloidal stability and imply complex microstructure effects linked to the partition of the not covalently bounded molecules between the water- and polymer-phases. It is worth to mention that the acrylated nature of the capping agent is not responsible in its own for the colloidal destabilization since butanol, although providing superior stability, is also limited using the selected temperature conditions.

The pH is a contributing factor of the colloidal stability as well as the selection of the neutralizing agent and, hence, the nature of the counter-ion. Higher pH values (usually above seven) are mandatory to guarantee an efficient surface charge

density capable to provide a good stability. Sodium counterions were found to be slightly better than triethylammonium counter-ions.

The chain extension with an aliphatic diamine provides a smaller particle size just after the dispersion, but is not recommendable to provide long-term colloidal stability.

It is becoming evident from this study that UV-PUDs constitute a waterborne polymer family with its own identity and that builds its complexity on top of the traditional radiation curing chemistry.

6. Perspectives

In order to extend our understanding of the systems studied in this work, additional experiments are being conducted with model dispersions cleaned by dialysis in order to remove undesirable interfering species present in the water phase. This dialysis methodology has been described elsewhere [18]. The end-capping agents include those already discussed in the present paper but also some pure model molecules (like hydroxyalkyl acrylates). The isolation of the surface charge density is approached with the determination of the ccc and with refined DLS experiments in order to observe slow coagulation kinetics following a methodology described elsewhere [19]. The zeta-potential can be determined from electrophoretic mobility measurements and can also provide complementary indications. All this should bring some light on the respective contribution of the polymer particle and that of the water phase.

The continuous enhancement of the colloidal stability on new polymer backbones by playing on some proprietary chemical modifications constitutes a key target for the future. In particular, the dispersion of polymers at higher solid content is a challenging diversification of these studies. High solid contents are interesting from a pure economical point of view since they limit the transport of water and the energy required to evaporate this water during the application of the product.

We are confident that the product robustness created by an improved colloidal stability will constitute a real competitive advantage for high-end waterborne polymers where performance and innovation are the major driving forces.

Acknowledgements

The authors wish to thank especially Vincent Renard and Marcus Vandermercken for their contribution in the synthesis of all the polyurethane dispersions.

Our study on colloidal stability was greatly facilitated by the successive graduation work of three students, Xavier Drooghaag (Institut Meurice, Belgium), Jean-Pierre De Backer and Steve Nyarwaya (Institut Supérieur Industriel de Bruxelles, Belgium).

At last, we wish to thank the many collaborators who contributed at a certain moment to this study and who still help us moving this extraordinary technology forward.

References

- [1] K. Tharanikkarasu, B.K. Kim, Aqueous dispersions of polyurethane ionomers, *Prog. Rubber Plast. Technol.* 13 (1) (1997) 26–55.
- [2] S.Y. Lee, J.S. Lee, B.K. Kim, Preparation and properties of water-borne polyurethanes, *Polym. Int.* 42 (1997) 67–76.
- [3] K.L. Noble, Waterborne Polyurethanes, *Prog. Org. Coat.* 32 (1997) 131–136.
- [4] M. Gerlitz, R. Awad, Taking to the water, *PPCJ* (2001) 34–37.
- [5] K. Buysens, M. Tielemans, Th. Randoux, Radiation curable coatings: a variety of technology for a variety of applications, *Pittura e Vernici – European coatings* 19 (78) (2002) 27.
- [6] M. Tielemans, V. Renard, S. Smeets, S. Piazza, J.C. Vanovervelt, New Perspectives for Radiation-Curable Polyurethane Dispersions, in: M. Tielemans, V. Renard, S. Smeets, J.P. Bleus, J.C. Vanovervelt (Eds.), *New Waterborne Radiation-Curable Polyurethanes for Wood and Plastic Materials*, 5, Forum de la Connaissance, Paris, 2003, pp. 36–44.
- [7] R. Schwalm, Cross-linking effect on mechanical properties of UV-curable coatings, *Polym. Paint Color J.* 189 (1999) 4421.
- [8] F. Masson, C. Decker, T. Jaworek, R. Schwalm, UV-Radiation curing of waterbased urethane-acrylate coatings, *Prog. Org. Coat.* 39 (2000) 115–126.
- [9] R. Satguru, J. McMahon, J.C. Padget, R.G. Coogan, Aqueous polyurethanes-polymer colloids with unusual colloidal morphological and application characteristics, *J. Coat. Technol.* 66 (1994) 830.
- [10] B.R. Saunders, B. Vincent, Microgel Particles as Model Colloid: Theory Properties and applications, *Adv. Colloid Interface Sci.* 80 (1999) 1–25.
- [11] A. Fernández-Nieves, A. Fernández-Barbero, B. Vincent, F.J. de las Nieves, Charge control swelling of microgel particles, *Macromolecules* 33 (2000) 2114–2118.
- [12] R. Hidalgo-Alvarez, A. Martin, A. Fernandez, D. Bastos, F. Martinez, F.J. de las Nieves, Electrokinetic properties, colloidal stability and aggregation kinetics of polymer colloids, *Adv. Colloid Interface Sci.* 67 (1996) 1–118.
- [13] R.M. Fitch, *Polymer Colloids: a Comprehensive Introduction*, Academic Press, London, 1997.
- [14] D.J. Shaw, *Introduction to Colloid and Surface Chemistry*, Butterworths, London, 1980.
- [15] I.W. Cheong, J.H. Kim, Synthesis of core-shell polyurethane-urea nanoparticles containing 4,4'-methylenedi-*p*-phenyl diisocyanate and isophorone diisocyanate by self-assembled neutralization emulsification, *Chem. Commun.* (2004) 2484–2485.
- [16] Personal communication & data from *Formulation* based on a model styrene-acrylic latex, see www.formulation.com.
- [17] M. Matsunaga, Y. Matsushima, H. Ohtani, S. Tsuge, Optimization of conditions for detailed compositional analysis of acrylic oligomers by supercritical fluid chromatography with temperature programming or modifier gradient technique, *Anal. Sci.* 17 (2001) 11.
- [18] G. Fritz, V. Schädler, N. Willenbacher, N.J. Wagner, Electronic stabilization of colloidal dispersions, *Langmuir* 18 (2002) 6381–6390.
- [19] L.H. Hanus, R.U. Hartzler, N.J. Wagner, Electrolyte-induced aggregation of acrylic latex I. dilute particle concentrations, *Langmuir* 17 (11) (2001) 3136–3147.