

Study of the rheology of aqueous radiation curable polyurethane dispersions modified with associative thickeners

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Abstract

The chemistry of radiation curable polyurethane dispersions is outlined with an emphasis on the microstructure of the aqueous polymer dispersion and the possible interactions with associative thickeners. The steady-shear flow was studied for two model dispersions prepared from the same unsaturated polyurethane but showing significantly different particle size distributions. A hydrophobically modified ethoxylated urethane (HEUR) associative thickener with a linear structure was incorporated at different amounts to the dispersions with varying particle volume fractions. The steady-state viscosity at 25°C and 10°C was always reached quickly after instant flow rate changes so that no significant thixotropic effects were reported within the experimental timescale. Without thickener, the flow curves of the two model dispersions exhibited a Newtonian behaviour except at the highest volume fractions where shear-thinning became apparent. The maximum packing values determined from the Krieger-Dougherty relationship were essentially the same for the two systems. In the presence of thickener, the flow curves were characterized by a Newtonian plateau followed by a marked shear thinning region even at low particle volume fractions. This behaviour typically suggests the formation of a physical network between polyurethane particles and thickener molecules partly adsorbed onto the polymer surface. The zero-shear viscosity of the two dispersions was compared with respect to (i) particle volume fraction and (ii) particle surface area at different HEUR concentrations. At a given volume fraction, the particle size affects the viscosity of thickened models. As a corollary, a relationship is found between the particles size and the level of thickener required to reach a target viscosity. This study offers practically relevant data in terms of application conditions and provides a better insight into the thickening protocol.

Introduction

The waterborne polymer technology is gradually conquering the industrial coating market as a consequence of a lower environmental impact coupled with innovative performance areas suitable to protect the substrates in challenging conditions [1]. Within this technology, radiation-curable polyurethane dispersions (referred to as UV-PUD) benefit from a favorable position due to their high-end performance and strong potential [2-3]. These products are frequently associated with a low volatile organic content (VOC) and a high productivity related to the rapid curing speed. The resulting coatings display excellent mechanical and chemical resistance for indoor [4-6] and outdoor [7] applications.

UV-PUD's are located at the boundary of different chemistries and technologies [8] and, hence, own their unique properties and advantages from *both* polyurethane polymers and radiation curing technology. At the same time, the colloidal nature of UV-PUD's differentiates them from their 100% counterparts to which they add a number of valuable and complementary features. As such, they contribute to sustain the growth in markets where the penetration of radiation curing is still low.

UV-PUD's are waterborne dispersions of unsaturated polyurethane particles, stabilized by the electrostatic repulsion of the negatively charged colloids [9,10]. The dispersion is in essence a metastable and heterogeneous, multi-phase system where the drifts from an ideal model underlines the morphological complexity [11-12]. The film formation is characterized by a 'minimum film formation temperature' (MFFT) that corresponds to the coalescence of the particles and the formation of a physically dry (tack-free) coating [13]. The nature of the polymer generally permits an easy film formation at low temperature without the necessary use of coalescing agents, which is very peculiar for waterborne polymer dispersions becoming very hard & resistant after the crosslinking process [14].

The low viscosity of UV-PUD's presents interesting perspectives (in comparison to their 100% equivalents) for application by spray, curtain or rolls. The rheology is not directly related to the molecular weight distribution of the dispersed polymer but is governed by (i) the volume fraction of the dispersed particles (ii) the particle size distribution and morphology (iii) the pH and the ionic strength of the aqueous phase [15]. Rheology modifiers are often used to adjust the flow and leveling properties of the dispersion in order to obtain a uniform, defect-free coating on the substrate.

Besides the wide range of rheology modifiers present in the market, the specific nature of the UV-PUD's imposes empirical formulation rules to tailor the rheological properties complying with the conditions of application [16]. The associative thickeners can confer many beneficial properties to the coating, such as improved formulation stability (e.g. no depletion flocculation) and better film formation, flow & leveling leading to gloss development. These performance benefits come at a price, however, as dispersions modified with associative thickeners tend to be more sensitive to formulation changes. This paper adds to the comprehension of the flow properties of radiation curable polyurethane dispersions modified with associative thickeners of the HEUR type. The nature of the thickener, the particle size of the dispersion and the temperature of measurement are the main variables of the study.

The rheology of aqueous polymer dispersions and associative thickeners

Polymer dispersions [17-19]

Many textbooks and papers describe the rheology of aqueous polymer dispersions. For the present study, a number of basic elements are briefly recalled. The flow of a liquid is often characterized by the dependence of the apparent viscosity $\eta = \tau \dot{\gamma}^{-1}$ with the shear stress (τ) and the rate of deformation ($\dot{\gamma}$). A constant viscosity corresponds to a Newtonian flow but shear thinning is common in polymer dispersions. The volume fraction of dispersed particles (ϕ) and the rate of deformation are fundamental variables of the flow behaviour. In the low shear rate regime, the steady shear viscosity shows a typical dependence with particle volume fraction. At low volume fractions, the flow is essentially Newtonian within the shear rate range covered by rotational rheometers. At higher volume fractions, but below the critical packing (ϕ_c), the viscosity curves exhibit a Newtonian plateau at low shear rates followed by a shear thinning region. The onset of shear thinning shifts to lower

shear rates and the degree of shear thinning increases with increasing volume fraction. Above the critical packing ($\phi > \phi_c$), the dispersions show a shear thinning behaviour over the full shear rate range which is characteristic of a gel-like state. In this regime, the shape of the flow curves hardly changes with particle density.

The volume fraction dependence of a wide variety of liquid dispersions is well described by the Krieger-Dougherty equation originally introduced to describe hard sphere suspensions

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-k} \quad (1)$$

where η_r is the viscosity of the dispersion relative to the viscosity of the continuous phase, ϕ_m is the maximum packing volume fraction and $k = 2$ for hard spheres in the low-shear limit. The divergence of the zero-shear viscosity is reminiscent of a transition from a disordered fluid to a glassy solid. For uniform hard spheres in dense random packing the value of ϕ_m is ≈ 0.63 - 0.64 . Extension to charged systems is straightforward using the excluded volume concept, introduced for the secondary electroviscous effect, which alters the maximum packing fraction according to

$$\phi_{m,eff} = \phi_m \left(\frac{d_{eff}}{d}\right)^3 \quad (2)$$

where d_{eff} and $\phi_{m,eff}$ are the effective particle size and maximum packing fraction of equivalent hard spheres, respectively.

The shear thinning effect in the liquid dispersion can be rationalized in terms of the Peclet number which measures the importance of the shear-induced force relative to that resulting from Brownian motion. Pe is defined by the relative rates of deformation and Brownian motion, *i.e.* $Pe \equiv \dot{\gamma} t_D$ where $\dot{\gamma}$ is the shear rate and t_D is a characteristic diffusion time. When, $Pe \ll 1$, Brownian motion dominates as the restoring force and the system behaves as if it were at equilibrium (*e.g.* in the zero-shear limit). In contrast, at $Pe \gg 1$, the shearing forces dominate, inducing an ordered dynamic structure, such as *e.g.* the formation of parallel sliding shear planes.

Associative thickeners [18, 20-24]

Associative polymer thickeners form a particular family of commercial organic rheology modifiers which includes naturally-derived and synthetic compounds. Hydrophobically modified ethoxylated urethanes (HEUR) belong to the latter class and are actually nonionic block copolymers where hydrophobic blocks have been attached, for instance, to polyethylene oxide polymers through urethane linkages. HEUR's can be telechelic or random block copolymers in linear or branched structures. The distinct rheological properties of HEUR's result from their amphiphilic nature. In an aqueous medium the hydrophobic groups will tend to associate in junction points. In most cases it is assumed that at relatively low concentrations, the polymers form micelles (flower-like for telechelic polymers) with a core composed of hydrophobic tails. At higher concentrations, hydrophobic groups of the same molecule can be incorporated in different micelles. The bridges between micelles gradually lead to large aggregate structures, eventually percolating in a (transient) 3-dimensional network at still higher concentrations.

The linear rheological behavior of telechelic associative polymers show a simple Maxwell behavior with a relaxation time related to the dissociation of the hydrophobe from the junction point. The relaxation of non-telechelic systems is more complex and characterized by a broad distribution of relaxation times.

In contrast to the relative simplicity of the linear properties, the non-linear rheological behavior in steady shear flow is far more complex. Typically, as the shear rate increases, solutions of telechelic polymers show a Newtonian plateau first followed by a weak viscosity increase and next by shear thinning at higher rates. The shear thinning can readily be assigned to shear-induced break-up of the gel structure. The weak shear thickening can be accounted for by a non-linear elastic behaviour of the

network strands that are stretched (strain-hardening). Shear-thickening would then be expected at shear rates just below those at which shear thinning occurs since highly stretched strands pull out of the micelles and destroy the network structure.

Radiation curable polyurethane dispersions

Many compositional variants have been described in the literature in order to obtain a stable colloidal dispersion of an acrylated polyurethane polymer suitable for application on several substrates.

In this study, we have used a composition and a process that includes the basic structural elements required to obtain a low molecular weight oligomer exhibiting properties and performances in line with commercial products, namely (a) a polyisocyanate (b) a polyol typically selected from polyester, polyether or polycarbonate diols in order to provide the flexible segments of the polymer (c) an hydrophilic polyol capable to disperse the polymer in water and to ensure its colloidal stability and (d) an unsaturated polyol bringing the crosslinking functionality.

A double-wall glass reactor equipped with a mechanical stirrer, a thermocouple, a vapor condenser and a dropping funnel is charged with (i) acetone, (ii) a polyester having a specific average molecular weight and obtained by the polycondensation of adipic acid with neopentylglycol, (iii) dimethylol propionic acid, (iv) 4,4'-dicyclohexylmethane diisocyanate and (v) dibutyltinlaurate - all being used within a specific {isocyanate}/{hydroxyl} equivalent ratio. The reaction mixture is heated up to reflux with stirring and the isocyanate content is followed by titration during the course of the synthesis. After the exotherm resulting from the reaction between isocyanate and alcohol, the reaction is kept under refluxing acetone until the isocyanate content reaches a target value. Then, (vi) 4-methoxyphenol dissolved in (vii) pentaerythritol triacrylate is added slowly to the vessel in a specific {hydroxyl}/{isocyanate} equivalent ratio. The reaction mixture is kept at reflux until the isocyanate content reaches a target value. The reaction mixture is cooled down to 50°C. The neutralization proceeds with (viii) triethylamine added to the hot pre-polymer in a specific {amine}/{carboxylic acid} equivalent ratio and mixed until homogenous. Then, the hot mixture is split in two parts and transferred slowly into (ix) two separate quantities of water at room temperature under high shear agitation until stable polymer dispersions are obtained at the target solid contents. The acetone is stripped out under vacuum and at a temperature of 50°C until the remaining level of solvent falls below 0.15%. The polymer dispersion is cooled down below 30°C and is filtered over a 100µ sieve. The solid content is adjusted to the target solid content by diluting with some water.

The characteristics of the two model dispersions are presented in Table 1. It is noteworthy that the dispersion of the same neutralized pre-polymer in two different amounts of water *in fine* delivers significantly different particle size distributions (108 nm at 45%, 47 nm at 35% as measured by dynamic light scattering). The differentiated aggregation of the particles during the dispersion and/or the solvent evaporation step (stripping) is invoked to account for this marked size difference.

The difference in particle size distribution for dispersions of identical oligomer composition provides a suitable test case to verify the effect of this variable on the rheological properties.

	Solid content (%)	Particle size (nm) ¹	pH	Viscosity, mPa.s
UV-PUD108	45	108 (0.16)	7.4	294
UV-PUD47	35	47 (0.06)	7.1	14

Table 1. Characteristics of the model dispersions

¹The particle size is reported as the z-average diameter from dynamic light scattering measurements. The polydispersity index is provided in brackets and indicates that the small particles are fairly monodisperse whereas the large particles are much more distributed.

The model structure of the UV-PUD is represented in Figure 1. The left side of the molecule is accountable for the end-capped polyurethane ($x = 1-3$, $z = 0$) while the right site between the large brackets represents the fraction of the polymers that have been naturally chain extended in water through the hydrolysis of the remaining isocyanates and the formation of an urea ($x = y = 1-3$, $z = 1$).

From this molecular representation, it is easy to recognize that these structures are true polyurethane oligomers having intrinsic hard urethane and urea domains with strong hydrogen bonding which, together with the acrylate crosslinking ability, give the material its hardness and resistance - whilst the softer domains serve as buffer zones and account for the flexibility and the elongation. As a consequence, an excellent balance in chemical resistance and mechanical properties

can be achieved due to the lower crosslinking density and the higher average molecular weight between crosslink points [14].

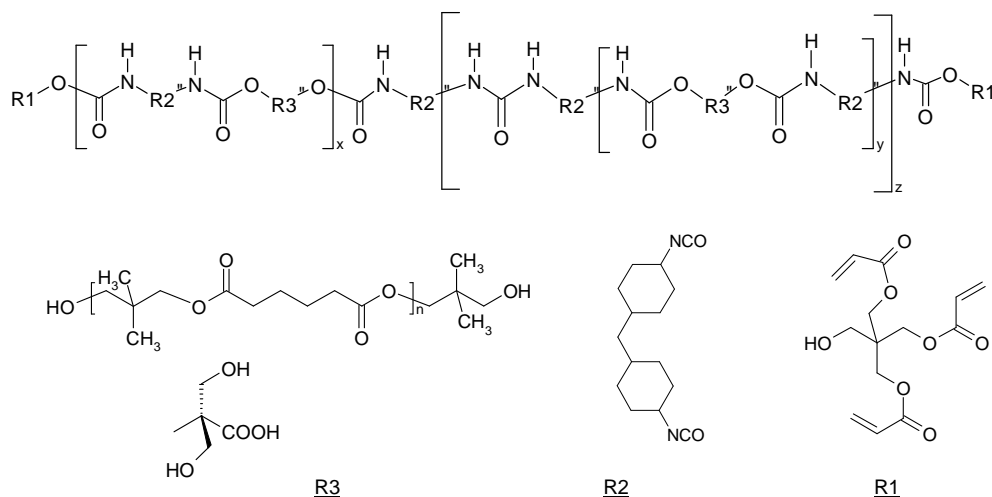


Figure 1. Structure of the model oligomers

The polyacrylate capping agents (like pentaerythritol triacrylate) are in fact complex mixtures of several reaction products from the polyol (like pentaerythritol) with acrylic acid used in such a stoichiometry and with such a process that a target hydroxylated molecule is prevalent [25]. This has several important consequences. On one side, there are deviations from the ideal oligomer structure depicted before since a distribution of higher molecular weights is accountable for the chain extension and chain branching obtained with the diol or polyol species. On the other side, there is a certain amount of acrylated molecules that do not contain any hydroxyl group and that will not covalently bond to the polyurethane oligomer. In the case of the dispersions of this article, we have estimated from the composition of the capping agent that there is about 85% of unsaturated polyurethane over 15% of free polyacrylated molecules.

A model colloidal dispersion is usually referred to as a system of uniform spherical particles of homogeneous particles. However, we have seen that several deviations from this ideal picture are possible. This has a significant impact on the complexity of the dispersion microstructure and all the related physico-chemical characteristics of the colloid, such as the rheology.

First, the particle can display heterogeneity of composition when going from the center to the outside of the particle, with a polymer-water interphase that is generally richer in ionic species: a typical morphology is then “gradient” or “core-shell” [11,12].

Secondly, the particles may reveal compositional, size and shape heterogeneities: particle size distributions can be multi-modal with composition variations between the populations. Also, small ionic telomers may be dissolved in the aqueous phase. In the present case where a small water-insoluble polyacrylated molecule is involved in significant amounts, this portion is likely to be distributed either in swollen polymer particles although the possible presence of independent droplets in a complex polyphasic system has not been excluded.

In this study, there was no further attempt to determine the microstructure of the dispersion otherwise than using dynamic light scattering measurements for the particle size distribution. There is little doubt that the study of the rheology of our model dispersions is influenced by complex microstructural effects that we keep as a perspective for further investigations.

Rheology modifiers

A linear telechelic (L) and a branched (B) polyether polyurethane thickener (HEUR) of the Additol range were supplied by Cytec Surface Specialties, Graz, Austria. They were provided as 30-35 wt% solution in a mixture of butyldiglycol and water. Due to the remarkable thickening properties,

only small quantities of HEUR were needed to modify the rheological characteristics of the UV-PUD. The amount of thickener is expressed as the weight ratio of dry HEUR polymer in the dispersion.

Rheological measurements.

The steady-state shear flow was measured with a stress-controlled Paar-Physica UDS 200 rheometer equipped with a concentric cylindrical system. Low and high viscosity samples were measured with a double-gap (22.25/22.75; 23.5/24.0 mm) and a single gap (12.5/13.56 mm) system, respectively. The sample was protected with a layer of mineral oil to avoid drying during analysis. Prior to any measurement, the sample was subjected to a shear rate $\dot{\gamma} = 10 \text{ s}^{-1}$ for 2 min followed by a recovery period at the lowest experimental shear rate. A period of 20 s was found to be sufficient for viscosity recovery. With this pre-shear protocol, the shear memory was equalized for all the samples. The flow curves were measured by increasing the shear rate (or stress) stepwise. At each step, the apparent viscosity was measured every second over a time interval of 20 s. As steady-state was reached within the first few seconds, the first two points were left out to compute the average for the steady-state viscosity.

Results and discussion

The two original dispersions with differentiated particle size (UV-PUD 108 and UV-PUD 47) have been diluted to target solid contents expressed as volume fractions and surface areas ($\text{m}^2 \text{ g}^{-1}$) in the plots. The rheological measurements were conducted at two temperatures (10 and 25°C) and in the presence of increasing amounts of associative thickeners (linear and branched). The most important results are discussed below.

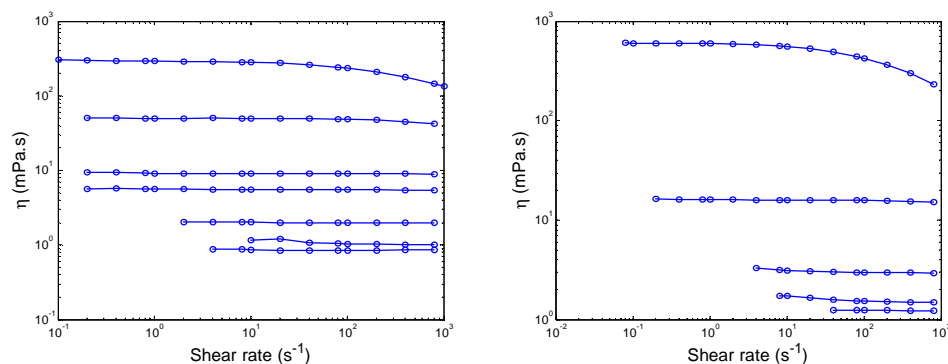


Figure 2. Steady-shear flow curve of UV-PUD108 as a function of particle content and temperature (25°C left, 10°C right). Left: 25 °C; $\phi = 0, 4.5, 18.5, 28.2, 33.1, 38.0$ and 43.1 vol%. Right: 10°C; $\phi = 0, 4.5, 18.5, 33.1$ and 43.1 vol%.

In Figure 2, the steady-shear flow behaviour of the UV-PUD with the large particles, *i.e.* UV-PUD108, is shown for particle volume fractions between 0 and 43 vol% at two temperatures, 25 and 10 °C. As discussed before, the curves are Newtonian in the dilute and semi-dilute regimes but become shear-thinning at $\phi > 0.35$. The steady state viscosity was reached quickly after instant flow rate changes so that no significant thixotropic effects were reported within the timescale of the experiments. A shift in temperature from 25 to 10 °C results in a twofold increase in viscosity. The behaviour is similar for the UV-PUD with small particles (UV-PUD47).

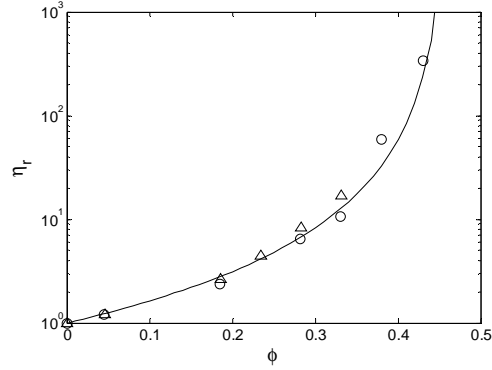


Figure 3. Zero-shear relative viscosity versus particle volume fraction. UV-PUD108 (circles) and UVPUD47 (triangles). The line results form a non-linear least-squares adjustment of the Krieger-Dougherty equation to the UV-PUD108-data.

The relative zero-shear (static) viscosity is plotted as a function of particle volume fraction in Fig. 3. The maximum packing is estimated from a non-linear regression of the Krieger-Dougherty expression, Eq. (1), to the data (the curve is shown for UV-PUD108 in Fig. 3). A value $\phi_m = 0.46$ and 0.44 is obtained for the large and small particle dispersion, respectively. The maximum packing is lower than expected for a randomly close-packed hard sphere assembly and actually reflects the presence of a double layer which increases the effective particle diameter. For a given surface layer thickness, the excluded volume will be higher for smaller particles which accounts for the somewhat lower maximum packing fraction of UV-PUD47.

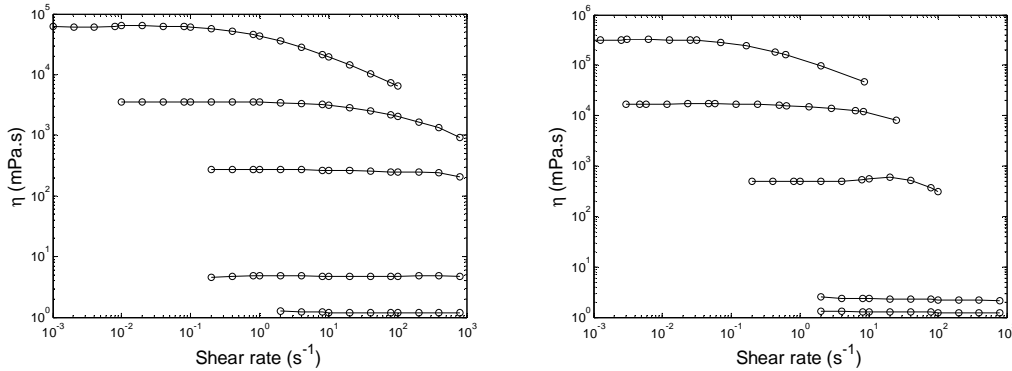


Figure 4. Steady-shear flow curves of UV-PUD108 after addition of 0.45 wt% of HEUR (25°C). Left: Linear HEUR; Right: Branched HEUR; $\phi = 0, 4.5, 18.5, 33.1$ and 43.1 vol%.

The addition of associative rheology modifiers dramatically modifies the flow behavior of the UV-PUD's. Figure 4 shows the effect after addition of 0.45 wt% linear (left plot) and branched HEUR (right plot) to UV-PUD108 at different particle volume fractions. For the linear HEUR, shear thinning appears within the experimental shear rate window at $\phi \approx 20$ vol%. At higher fractions, the shear thinning region is more pronounced and the onset shifts to lower shear rates. Introduction of the branched HEUR results in higher viscosity enhancement as compared to the linear one. Noteworthy, shear thickening is even detected before shear thinning at a volume fraction $\phi = 18.5$ vol%. This feature provides clear evidence that the HEUR polymers and the colloidal particles form a structural network. It is often assumed that the hydrophobic tails of the HEUR molecules partly adsorb on the particle surface and act as bridges between HEUR micelles and particles or between particles. From this perspective, it is straightforward to think that branched molecules will promote network formation as compared to linear compounds. At this stage, it is also interesting to point out that the flow

behaviour could not be measured for the most viscous dispersions at high shear rates due to wall slip and even shear fracture. Again, no significant thixotropic effects were reported within the timescale of the experiments.

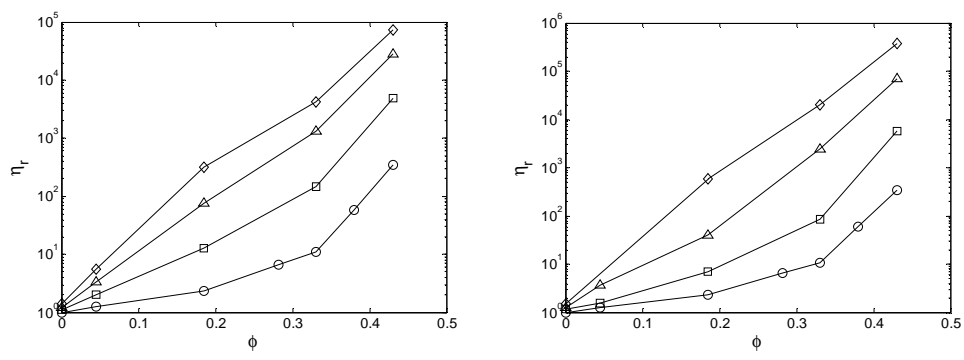


Figure 5. Relative zero-shear viscosity vs. particle volume fraction for UV-PUD108: effect of HEUR content; 0 wt% (circles), 0.15 wt% (squares), 0.30 wt% (triangles) and 0.45 wt% (diamonds). Left: linear HEUR; right: branched HEUR (25 °C).

In Figure 5, the relative zero-shear viscosity is plotted versus particle volume fraction at 0, 0.15, 0.30 and 0.45 wt% HEUR. In water, these levels of HEUR result in weak viscosity increases which suggest that the molecules are assembled in small entities (e.g. micelles) with loose or even no interconnections. However, small volume fractions of dispersed particles give rise to substantial viscosity enhancements which increase markedly with particle and HEUR content. Without rheology modifier, the concentration dependence of the zero-shear viscosity is characterized by an asymptotic behaviour at high particle loadings, typical for particle suspensions. Incorporation of the associative rheology modifier progressively moves this behavior to a more linear trend which suggests that beyond some thickener content, the rheological properties are governed by the structure and the dynamics of a transient network.

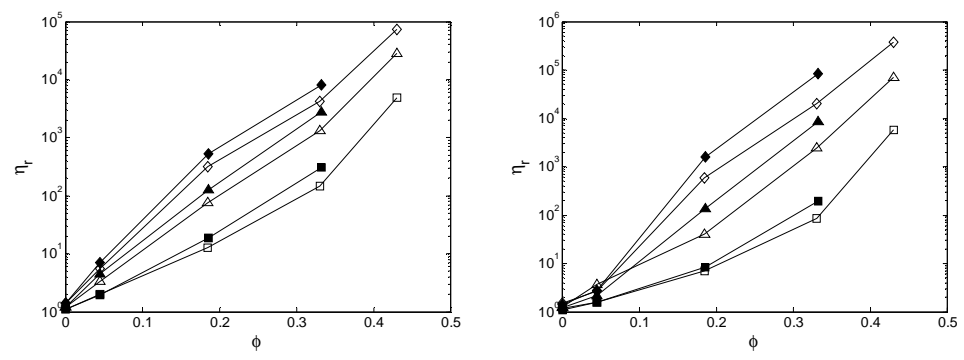


Figure 6. Relative zero-shear viscosity vs. particle volume fraction (25°C): effect of particle size; UV-PUD47 (solid symbols) and UV-PUD108 (open symbols). Left: linear HEUR; right: branched HEUR. Symbols for HEUR content similar as in Fig. 5.

The effect of particle size is illustrated in Figure 6 and shows that in general, the static viscosity of UVPUD47 is higher as compared to UVPUD108 in the overlapping particle concentration range. By plotting the relative difference in static viscosity between the two UV-PUD, the variations due to marked size changes are highlighted at the various HEUR levels (Fig. 7). Noticing the relative viscosity difference of $\approx 45\%$ without rheology modifier, we see that it is amplified to $\approx 70\%$ for the linear HEUR whereas it rises to $\approx 120\%$ for the branched system.

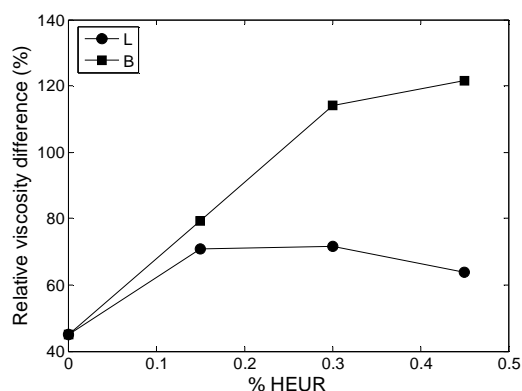


Figure 7. Relative difference between the zero-shear viscosity of UVPUD47 and UVPUD108 at 35 wt% as a function of HEUR content (25 °C).

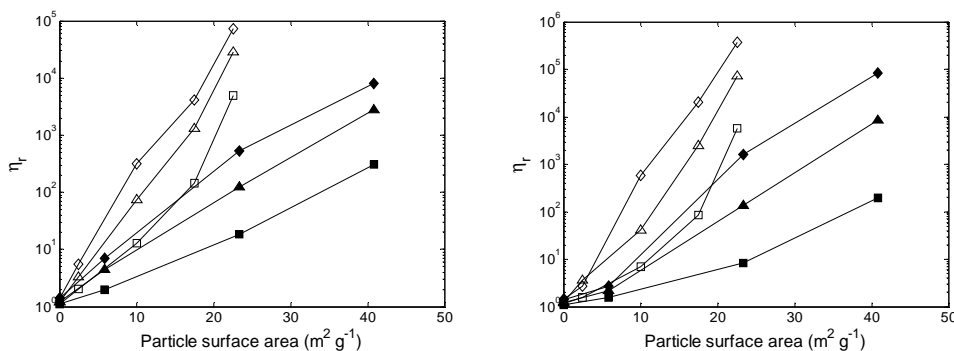


Figure 8. Relative zero-shear viscosity vs. particle surface area (25°C): UV-PUD47 (solid symbols) and UV-PUD108 (open symbols). Left: linear HEUR; right: branched HEUR; 0.15 wt% (squares), 0.30 wt% (triangles) and 0.45 wt% (diamonds).

It is instructive to plot the relative zero-shear viscosity as a function of particle surface area per unit mass of liquid dispersion. In Fig. 8, the particle surface area represents the surface area in contact with the aqueous phase at a given particle loading and is calculated from the particle weight fraction, the particle density and the average particle size. It is observed that the relative viscosity increases with HEUR content at a fixed value of surface area and suggests that more HEUR molecules are adsorbed at the particle surface, as expected. However, for particles of different sizes the viscosity levels are quite different. As long as the particulate nature of the dispersion dominates the rheology (e.g. 0.15 wt% HEUR), this difference is easily rationalized based on the similarity of the curves in Fig. 3 (after transformation of the x-axis to surface area units). However, when the network structure of the thickened dispersion becomes predominant, one expects that the trend would overlap for particles of different sizes. At a HEUR content of 0.45 wt%, there is no match between the curves of UV-PUD180 and UV-PUD47 and the slope of the former is much higher. It is inferred that either (i) the rheology is not fully controlled by the structure and dynamics of the network, (ii) or that the adsorption of HEUR molecules is not simply proportional to the accessible surface area but also depends on its nature, (iii) or that the particle surface area based on the average size is underestimated for UV-PUD180 (iv) or a combination of these factors. Point (iii) is appealing because it supports the assumption that the particles of UV-PUD180 are non-spherical with an irregular shape due to possible aggregation of smaller particles. In this case, the surface area based on the DLS particle size is underestimated. The ratio of the slopes for the curves with 0.45 wt% HEUR in Fig. 8 then indicates that the effective surface area for UV-PUD180 is about 1.5 to 2.5 higher than the value provided on the x-axis.

Conclusions

The radiation-curable polyurethane dispersions described in this study present a low viscosity that makes them particularly recommendable for application by spray, roller and curtain. They reveal however a complex micro-structure that influences directly their rheological behavior in the presence of associative thickeners.

The flow of two model dispersions with different particle size distributions was studied as a function of particle volume fraction and follows a behavior typical for interacting colloids that can be described by an equivalent hard sphere model. The rheology of the dispersions is Newtonian up to volume fractions of ≈ 0.35 and no thixotropic effect is observed within the timeframe of the experiments. As expected, temperature significantly affects the rheological behaviour.

The addition of increasing amounts of associative thickener has a pronounced effect on the zero-shear viscosity of the dispersion. The rheology data suggest the formation of a transient physical network including the polymer particles at high volume fractions. Associative thickeners with a branched structure lead to higher viscosities as compared to linear compounds likely due to the formation of a denser network. Plots of the zero-shear viscosity as a function of particle surface area further reveal that particle surface characteristics, such as the topology and the polarity, may alter the network properties.

The size distribution and the morphology of the particles dramatically affect the zero-shear viscosity of thickened dispersions at a given volume fraction and pH. As such, this observation accounts for the variance in the zero-shear viscosity resulting from the thickening of dispersions having particle size distribution fluctuations inherent to the capability of an industrial dispersion process.

Finally, this study offers new perspectives for a more rational approach of the formulation of UV-PUD's with associative thickeners by modeling the relation between target viscosity and thickener level as a function of solid content, mean particle size and pH.

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