The Relationship between Rheological Properties and Spraying Behavior of Polymer Dispersions

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Summary: The influence of the rheological properties on the spraying behavior of an adhesive polyurethane dispersion modified with different thickeners was investigated. The differences in shear rheology for the three different kinds of thickeners were found not to be representative for the spraying behavior. The extended fan sheets and reduced overspray for the water-soluble thickener correspond to a more pronounced elastic rheological behavior of the dispersion.

Keywords: adhesives; dispersions; elongational viscosity; spraying; thickener

Introduction

The application viscosity of solutions of polyurethane in organic solvents is dominated by the molecular weight of the polymer. In contrast, the viscosity of polyurethane dispersions is independent of the molecular weight of the polymer within the latex particles. The rheological properties of such dispersions can be adjusted by means of rheology modifiers such as water-soluble and associative thickeners.[1]

Numerous research groups have investigated the rheology of associative polymer systems. The review by Winnik and Yekta[2] and the work of Larson[3] provide a detailed survey of this literature. The influence of associative thickeners on particle interaction and the contribution of the dispersion viscosity are described by Reuvers.[4] The rheology of associative polymers in shear and extension has been studied recently by Tripathi et al.[5] They investigated the experimental and theoretical transient extensional stress growth behavior of a series of model hydrophobically modified ethoxylate-urethane (HEUR) polymers using a filament stretching rheometer.

Due to the advantages in flow and leveling properties and spatter resistance of low molecular weight associative thickeners for latex coatings, the influence of other water-soluble, high molecular weight thickeners such as cellulosic polymers, polyvinylalcohol, polyvinylpyrrolidone, polyethylene oxide and polyacrylics are documented to a much lesser degree in the scientific literature.[6,7]

With Newtonian fluids, viscosity and surface tension determine the spray behavior. The influence of these parameters on spray behavior has been described by several authors. Examples of review papers are Lefebvre[8] and Snyder.[9] These investigations show that during the collapse of a fluid film, mean particle diameter increases with increasing viscosity, and a decrease in surface tension leads to a decrease in mean particle diameter. The spraying behavior of viscoelastic fluids is much more complicated.[10] Capillary break-up extensional rheometers (CaBER,[11]) are now commercially available to measure the elongational viscosity of low-viscosity elastic fluids.

In this presentation, the influence of different thickener systems on the spraying behavior of polyurethane adhesive dispersions is investigated. Capillary break-up rheometry is used to determine the exten-

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sional viscosity and compare it with shear rheological data.

Experimental Part

The latex dispersion used is a commercial polyurethane Dispercoll latex from Bayer MaterialScience. Dispercoll is a waterborne polyurethane dispersion used as a raw material for adhesive applications, with a mean latex particle diameter of about 150 nm and 40% solid content. Three different types of thickener at weight concentrations of 0.5, 1, 2, 4 and 10% were used: Borchigel L75N, an associative polyurethane thickener; Borchigel ALA, a water-soluble polyacrylate (Borchers, Germany); and Collacral VAL, a water-soluble polyvinylpyrrolidone from BASF. IR analysis showed that the Borchigel ALA is an ammonium-polyacrylate, and GPC measurements showed that Borchigel VAL is a polyvinylpirrolidone-polyacrylate. The molecular weight of the samples diluted in water was determined by means of GPC with Shodex-OH B803-806 columns. The molecular weight M_w of Borchigel ALA was found to be about $4\ 10^5$ kg/kmol and the molecular weight of Collacral VAL about $2\ 10^4$ kg/kmol.

The steady shear viscosity was determined in a Paar Physica UDS200 rheometer at 25 °C. The shear rate was first increased exponentially from 0.1 to 1,000 1/s, and then decreased exponentially from 1,000 to 0.1 1/s. Oscillatory shear experiments were performed with a Bohlin CS50 rheometer.

The extensional viscosity was determined with a capillary break-up rheometer designed and built at the University of Erlangen-Nürnberg.[10] The break-up profile of each sample was determined at least five times for statistical reasons.

The surface tension of the dispersions was determined by means of a Kruess Processor Tensiometer K12 at 23.8 °C.

The equipment to study the spraying behavior was developed at the University of Dortmund. Images of the spray fan were recorded by means of a Vistek video camera in combination with a stroboscope light with 1,400 flashes per minute (Drelo Stroboport 1007) For the spraying experiments, a 0.4 mm 60° airless nozzle was used at pressures up to 30 bar.

Results and Discussion

Paints that use entangled high molecular weight polymers to increase viscosity usually have high extensional viscosities, which produce spatter during roller application. In contrast, associative thickeners do not have high extensional viscosities because the network structures formed by polymer-polymer or polymer-latex associates are destroyed when the network is elongated.[12] For some applications of latex dispersions, however, a high extensional viscosity is favorable. Dispersions with high extensional viscosity can be applied by airless spraying almost without any overspray. Especially for adhesives, the optical properties caused by the leveling behavior are much less important than, for example, in automotive coatings. The well-defined spraying angle allows highly precise application of the adhesive, e.g. to shoe soles, wood panels or furniture foam constructions.

Associative thickeners are water-soluble or water-dispersible polymers that feature both hydrophilic and hydrophobic moieties within the same polymeric molecule. The hydrophobic segments of the molecule are capable of forming intermolecular associations and adhering to the surface of the dispersed latex particles in the system. The thickening and rheology provided by this modification mechanism is much greater than is achieved with unmodified polymers of equal molecular weight. Disadvantages of associative thickeners include hydrolytic instability, phase separation, sensitivity to formulation changes and pH dependence.[12]

Acrylic acid thickeners consist of an acrylic backbone and pendant carboxylic acid groups. When dispersed in aqueous media, and while the system is acidic, they produce minimal rheological effects, but when the pendant carboxylic groups are neutralized with an alkaline ingredient, the polymer is said to "swell," producing a dramatic viscosity increase and rheological modification.[7]

Polyvinylpyrrolidone (1-ethenyl-2-pyrrolidoinone homopolymer) is a water-soluble polymer. In its pure form, PVP is so safe that not only is it edible for humans, it was even used as a blood plasma rheological modifier for trauma victims in the mid 20th century. In solution, it has excellent wetting properties and readily forms films.

An indication of the spraying behavior can be seen in Figure 1a)–c), which show the spraying behavior of the polyurethane dispersion with 2 wt.% of thickener at a pressure of 3 bar. At this low pressure, a smooth film filament can be seen at the nozzle. At larger distances from the nozzle, the film becomes wavy, and finally the wavy film breaks up into fluid filaments and droplets. The onset of the break-up of the smooth film changes with the pressure applied. At a pressure of 15 bar, a film fluid can no longer be detected (see Figure 2). Figure 1 shows that the water-soluble, high molecular weight thickeners dramatically change the spraying behavior, whereas the low molecular weight associative thickener cause only minor changes in spraying behavior.

The shear viscosity shows a relatively large hysteresis for the sample modified with the associative thickener (Figure 3), whereas the copolymer yields only a minor hysteresis. The water-soluble polymer does not show any hysteresis at all. Figure 4 shows the shear viscosity of all samples as a function of the shear rate. At low shear rates, 4% by wt. of thickener in the latex (i.e. 6.7% of thickener in serum) raises the viscosity of the latex by a factor of between one hundred and one thousand. The associative thickener shows a plateau in viscosity at lower shear rates, whereas the higher molecular weight, water-soluble polymers show a steady increase in viscosity with decreasing shear rate. The viscosity of the latex thickened with the Borchigel ALA polyacrylate thickener is higher than that of the sample modified with the Collacral VAL polyvinylpyrrolidone. The same amount of thickener in water gives completely different results. Only the polyacrylate Borchigel ALA thickener raises viscosity dramatically. This indicates that both the associative thickener Borchigel L75N and polyvinylpirrolidone Colla-

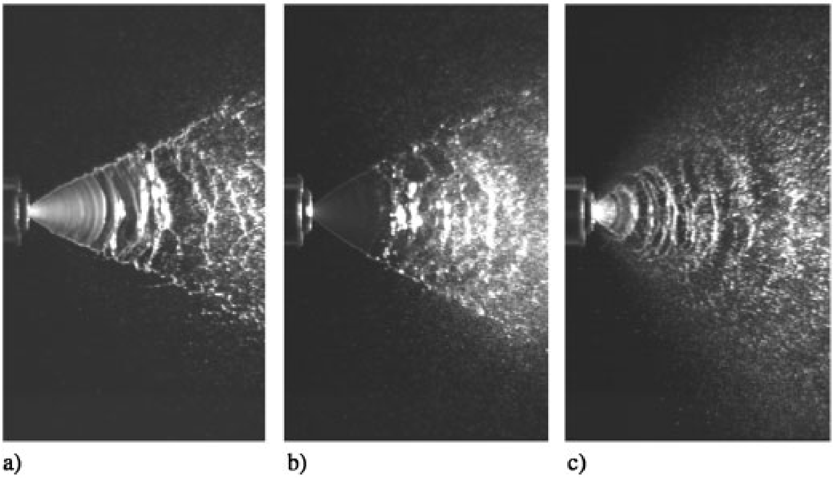

Figure 1.
Spraying behavior of latex with 2 wt.% thickener a) Borchigel ALA, b) Collacral VAL; c) Borchigel L75N — 25 mm.

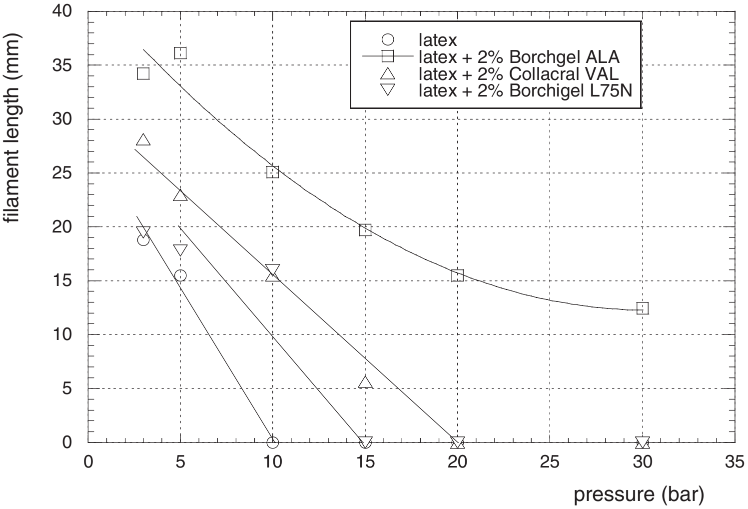

Figure 2.
Fan sheet or filament length of latex with 2% by wt. thickener as a function of the pressure applied.

cral VAL strongly interact with the latex particles, whereas the polyacrylate Borchigel ALA changes the viscosity of the serum and has only little or no interaction with the latex particles.

Dispersions with high extensional viscosity can be applied by airless spraying almost without any overspray.[10] The ratio of elongational to shear viscosity gives us an indication of the influence of elasticity of the fluid on the spraying behavior. Unfortunately, measurements with the capillary break-up extensional rheometer (CaBER) were possible for only some of the modified dispersions. Most of the samples had a viscosity either so low that the time during which a fluid filament was formed was too short, or they had a higher viscosity but no

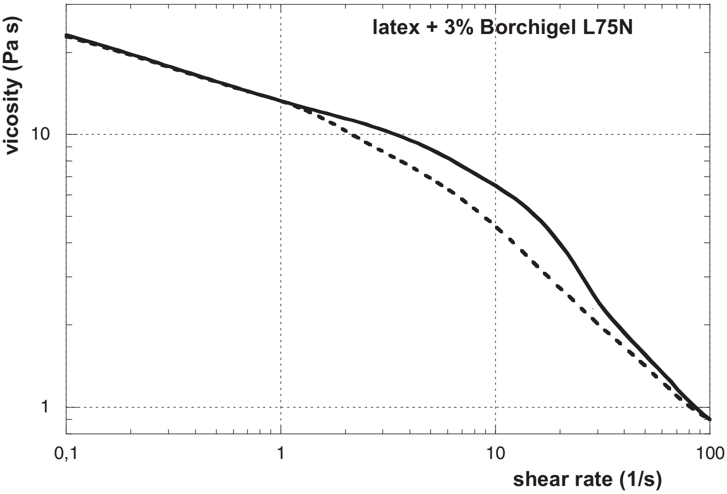

Figure 3.
Hysteresis in the viscosity as measure from low to high shear rate (full line) and from high to low shear rate (dotted line).

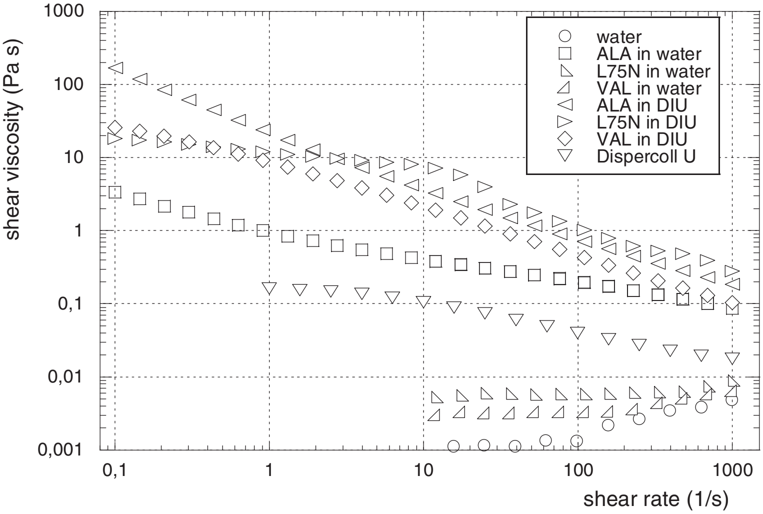

Figure 4.
Shear viscosity of water and latex modified with 6.7% by wt. in water (i.e. 4% in dispersion with 40% solid state) of Borchigel ALA; Collacral VAL; Borchigel L75N.

measurable fluid filament. These high viscosity samples showed no continuous decrease in filament diameter during the experiment. Instead of a filament with homogeneous diameter, necking of the sample was observed (Figure 5). Although the samples did not deform in the appropriate way for this measurement method, the results for those samples that could be measured yielded acceptable results (Figure 6). For those samples where oscillatory rheometry yielded Newtonian behavior a transient elongational viscosity was found that was three times the value of the transient shear viscosity (Trouton ration).

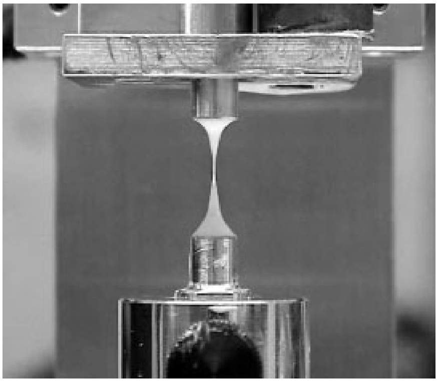

Figure 5.
Photograph of the necking of the sample in the capillary break-up extensional rheometer (CaBER).

Another possible way to investigate the elasticity of the thickened dispersions is given by oscillatory measurements. The storage modulus gives the elastic fraction, and the loss modulus gives the viscous fraction. Figure 7 shows the storage modulus of the latex dispersion with 1 and 3 wt.% thickener. The storage modulus values of a pure latex sample at the highest frequencies might be a little bit too low due to inertia effects of the double gap geometry. Figure 7 shows that the water-soluble polyacrylate thickener causes a large increase in storage modulus, whereas the polyvinylpyrrolidone thickener causes only a small increase. As expected, the associative thickener did not yield any increase in storage modulus at all. The storage modulus as measured in oscillatory shear seems to be a good indication for the elasticity of the sample and its influence on the flow behavior as can be seen in atomization and spraying.

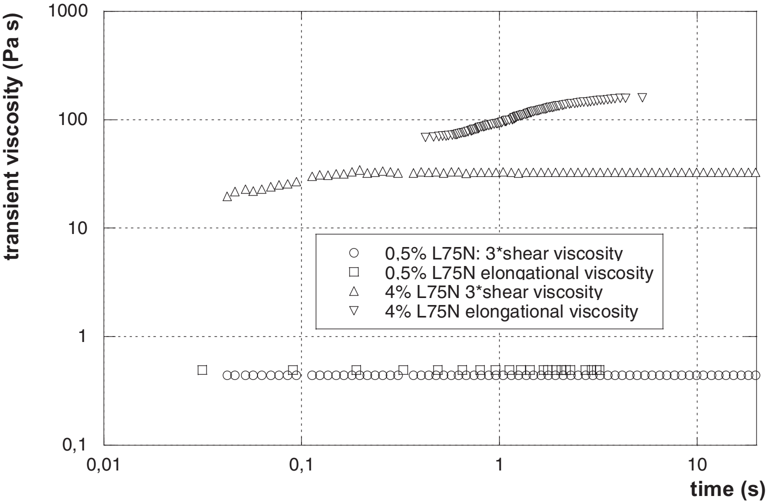

Figure 6.
Transient viscosity as measured from CaBER data compared to start up shear viscosity multiplied by the Trouton ratio.

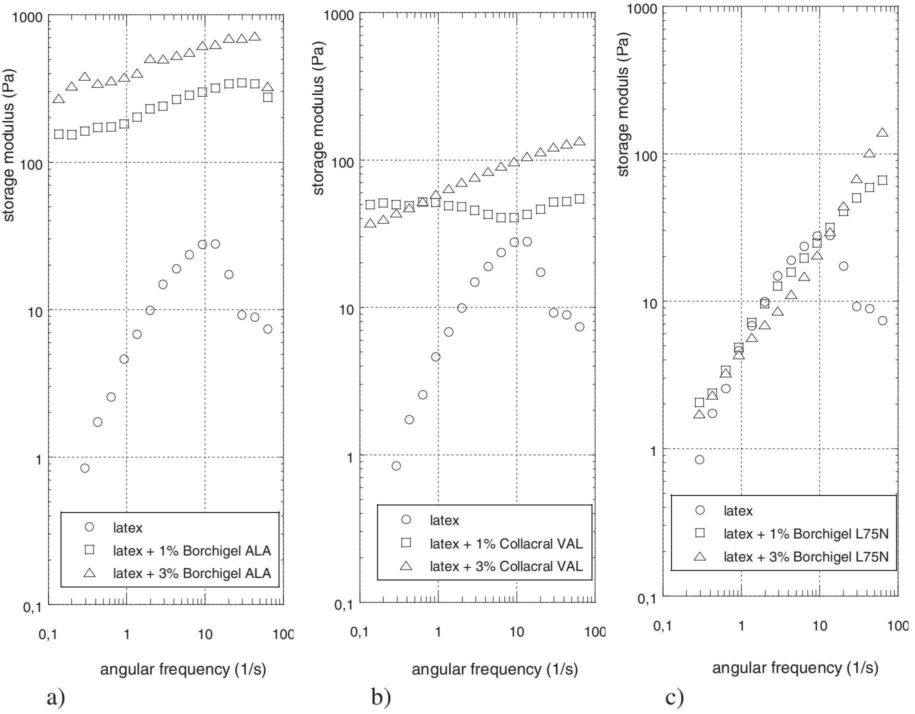

Figure 7.
Storage modulus as a function of the angular frequency for latex thickened with 1% and 3% a) Borchigel ALA; b) Collacral VAL; Borchigel L75N.

Conclusions

The influence of the rheological properties on the spraying behavior of an adhesive polyurethane dispersion modified with three different kind of thickeners was investigated. A high molecular weight, water-soluble polymer, a copolymer with a hydrophilic and a hydrophobic component, and a low molecular weight associative thickener were chosen to demonstrate the effect of the interaction of the thickener with the latex particles on the viscoelastic properties and spraying behavior. The differences in shear rheology for the three different thickeners were found not to be representative for the spraying behavior. The associative thickener showed only minor changes, whereas the higher molecular weight, soluble thickeners changed the spraying angle and the amount of overspray dramatically. Determination of the elongational viscosity by means of the CaBER rheometer proved to be of limited use for thickened dispersions. Oscillatory rheometry proved to be a more appropriate method for measuring the elastic properties of these thickened dispersions. The storage modulus measured in oscillatory investigations corresponds to the length of the extended spray fan and the reduced overspray found in the spraying experiments.

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