The Relationship between Rheological Properties and Spraying Behaviour of Polymer Dispersions

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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 the 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 behaviour of a series of model hydrophobically modified ethoxylate-urethane (HEUR) polymers using a filament stretching rheometer.
Due to the advantages in flow and levelling properties and spatter resistance of low molecular weight associative thickeners for latex coatings, the influence of other water-soluble high molecular weight thickeners like cellulosic polymers, polyvinylalcohol, polyvinylpyrrolidone, polyethylene oxide and polyacrylics are much less documented in the scientific literature [6, 7]
With Newtonian fluids, the viscosity and surface tension determine the spray behaviour. The influence of these parameters on the spray behaviour 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, the mean particle diameter increases with increasing viscosity and a decrease in surface tension leads to a decrease in mean particle diameter. The spraying behaviour 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 behaviour of polyurethane adhesive dispersions is investigated. Capillary break-up rheometry is used to determine the extensional viscosity and to compare this with shear rheological data.

Experimental

The latex dispersion used is a Dispercoll U53 from Bayer MaterialScience. This is a water-borne polyurethane dispersion used as a raw material for adhesive applications, with a mean latex particle diameter of about 150 nm. 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.
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 1000 1/s, and then decreased exponentially from 1000 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, for statistical reasons, determined at least five times.
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 behaviour was developed at the University of Dortmund. Pictures of the spray fan were made by means of a Vistek video camera in combination with a stroboscope light with 1400 flashes per minute (Drelo Stroboport 1007) For the spraying experiments, a 0.4 mm 60° angle airless nozzle was used at pressures up to 30 bar.

Results and discussion

Paints which 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 levelling behaviour 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 after the first half of the 20th century. In solution, it has excellent wetting properties and readily forms films.

An indication of the spraying behaviour can be seen in Figures 1 to 4. In Figure 1 the spraying behaviour of the polyurethane dispersion without any modification is shown at different pressures. At low pressure, a smooth film filament can be seen underneath the nozzle. At larger distances from the nozzle, the film becomes wavy and finally the wavy film is broken 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. Figures 2, 3 and 4 show that the water-soluble high molecular weight thickeners dramatically change the spraying behaviour, whereas the low molecular weight associative thickener shows only minor changes in spraying behaviour compared with Figure 1.

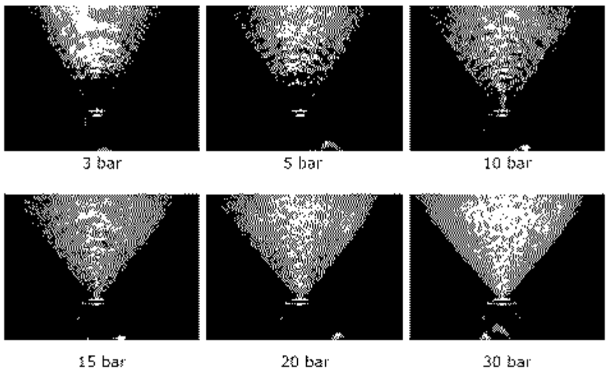

Figure 1. Spraying behaviour of the Dispercoll U53 latex without thickener —— 30 mm

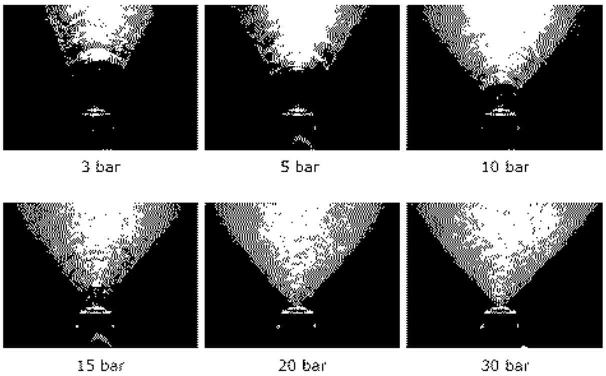

Figure 2. Spraying behaviour of the Dispercoll U53 latex with 2% by wt Collacral VAL polyvinylpyrrolidone thickener

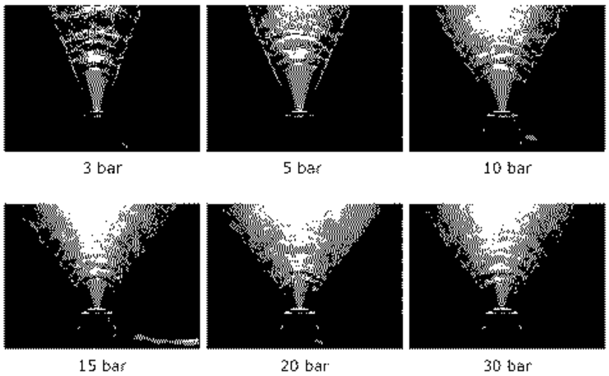

Figure 3. Spraying behaviour of the Dispercoll U53 latex with 2% by wt Borchigel ALA acrylic thickener

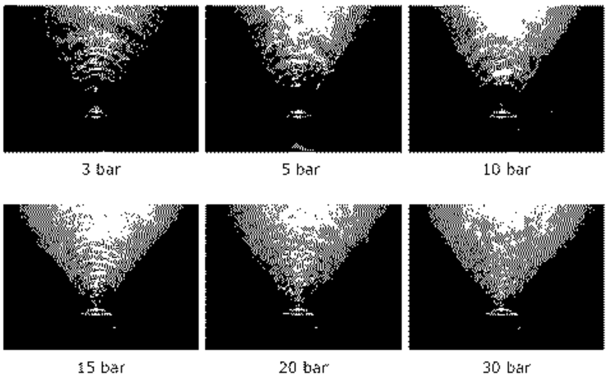

Figure 4. Spraying behaviour of the Dispercoll U53 latex with 2% by wt Borchigel L75N associative thickener

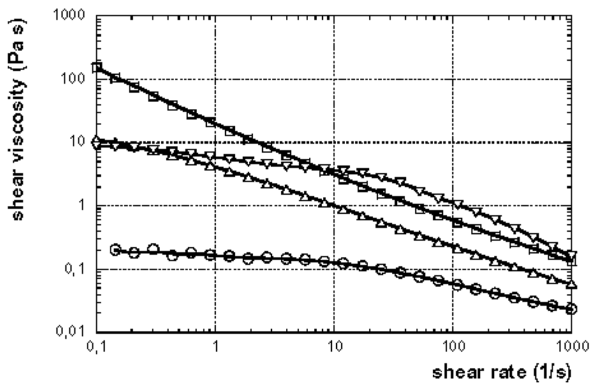

Figure 5. Shear viscosity of Dispercoll U53 modified with 2% by wt of: (○) without modifier; (□) Borchigel ALA; (△) Collacral VAL; (▽) Borchigel L75N

Figure 5 shows the shear viscosity in relation to the shear rate. At low shear rates, 2% by wt. of thickener raises the viscosity by a factor of between one hundred and one thousand. The associative thickener shows a plateau in the 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 sample thickened with the Borchigel ALA polyacrylate thickener is higher than that of the sample modified with the Collacral VAL polyvinylpyrrolidone.

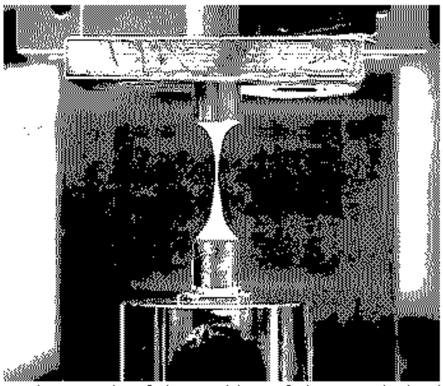
Figure 6. Photograph of the necking of the sample in the capillary break-up extensional rheometer (CaBER)

Measurements with the capillary break-up extensional rheometer (CaBER) were only possible for 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 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 6).

Conclusions

The influence of the rheological properties on the spraying behaviour of an adhesive polyurethane dispersion modified with different thickeners was investigated. The differences in shear rheology for the three different thickeners were found not to be representative for the spraying behaviour. 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.

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