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Enhancing deposition of agricultural sprays by the use of polymeric adjuvant

Master of Science Thesis

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Abstract

There is a growing demand for a more efficient farming due to a growing world population as well as reduced area of arable land. One way to obtain larger yield is to use pesticides, however the amount of pesticide has traditionally been overdosed vastly since there is a problem for the pesticide to reach its site of action. One way to increase the bio efficacy is to add adjuvants, which is a comprehensive term for additives that increases the bio efficacy of the pesticide solution. One of the major problems during crop spraying is the difficulty to make pesticide droplets to adhere to plant leaves; usually less than 50 % of the droplets are retained. By using polymers with high elongational viscosity the deposition can be increased.

The aim of this thesis is to increase the knowledge and understanding on how polymers can enhance deposition onto hydrophobic surfaces and how polymer-surfactant interaction influence deposition and droplet size upon atomization. Since there is a growing demand for green chemicals, the focus in this thesis lies on polymers based on cellulose.

The tested polymers increase the deposition of aqueous solutions on hydrophobic surfaces. The deposition effect is correlated to the elongational viscosity for all polymers but one. The characteristics of the polymer, as well as the concentration are determining the deposition enhancing effect. Addition of polymers to a solution containing a currently used pesticide adjuvant, a surfactant, has shown to increase the deposition.

Table of Contents

Introduction	1
Theory	2
Application.....	2
Polymers	3
Cellulose	3
Controlling droplet size and deposition	4
Rheology.....	4
Dynamic surface tension.....	6
Polymers and surfactants	6
Materials and Methods	9
Materials	9
Static surface tension	9
Dynamic surface tension.....	10
Rheology.....	10
Drop test – tilting plane.....	10
Drop test – droplet retraction	11
Worthington jet.....	11
Droplet mass	12
Results and discussion	13
Rheology	13
Droplet impact	18
Polymer and surfactant	22
Worthington jet.....	26
Conclusion	27
Future work	28
Acknowledgement	29
References	30

Introduction

Annually, more than 10 billion MT of crops are produced globally to feed the population of the world (FAO 2006) and the agrochemicals sales have a value of more than 10 billion Euros yearly (Phillips McDougall 2007). In the last decades, there has been a focus to increase the productivity of agriculture, due to an increasing world population as well as a reduced area of arable land, i.e. spreading of urban areas, infrastructure and deserts. Traditionally the way to solve this dilemma has been to use pesticides to reduce the competition from weeds as well as reducing the effects of fungus and insect attacks. Traditionally the amount of pesticides has been vastly overdosed since there is a problem for the pesticide to reach its site of action. The idea of quit using pesticides is not an option since this would reduce the crop yield to approximately 50% (Bergström et al. 2008) and in some cases the whole harvest can be lost, e.g. fungus attacks on potato plants. One way to increase the bio efficacy of pesticides and thereby reduce the amount of pesticides sprayed onto the fields is to add adjuvants. An adjuvant is usually a surfactant, a polymer or an oil that increases the bio efficacy whether it stabilizes the formulation, makes droplets to stay on the plant leaves, makes the spray droplets resistant to rain or drying or if it helps to penetrate the wax layer of the plant leaves.

One major problem during crop spraying is the difficulty to make droplets, sprayed from a nozzle, to adhere to a hydrophobic plant leaf; usually less than 50 % of the pesticide solution is retained on the plants during the deposition step (Bergeron et al. 2000; Bergeron 2003). By controlling the surface chemistry and the rheology of the pesticide solution the effectiveness can be increased. Some types of polymers have been shown to increase the deposition of aqueous solution on hydrophobic surfaces.

The aim of this thesis is to increase the knowledge and understanding on how polymers can enhance deposition onto hydrophobic surfaces and how polymer-surfactant interaction influence deposition and droplet size upon atomization.

Since there is a growing interest of green chemicals the majority of the studied polymers are based on the biopolymer cellulose, which is a naturally occurring polymer that is biodegradable. The chemical modification of the cellulose, that is necessary, however requires chemicals that today are produced from fossil raw materials. A cationic polymer will be tested and compared with the cellulose based polymers. Properties such as elongational viscosity, shear viscosity, dynamic surface tension and droplet impact behavior onto hydrophobic surfaces are studied.

Theory

Application

Crop spraying can be divided into several steps, see figure 1. The first thing that happens during crop spraying is the actual spraying and the following atomization. The time scale for the atomization is 4-5 ms according to Wirth et al. (Wirth et al. 1991) and 1-20 ms according to Dexter (Dexter 1996). The next step is the trajectory, the transportation from the nozzle to the plant leaves, and the time scale for this is 100-400 ms (Wirth et al. 1991). The weather has a big impact on this step; if it is windy the droplets will drift, possibly hit off target. The drift affects smaller droplets to a larger extent, since they aren't affected as much by gravity (Bergeron 2003). The time it takes for the droplets to be transported from the spray nozzle to the plants is 2 seconds for a coarse spray with a droplet diameter of 400 μm , 6 seconds for a medium spray where the droplet diameter is 240 μm and 4.2 minutes for a very fine spray where the droplet diameter is 20 μm (Bergeron 2003). When a droplet hits a plant leaf it can either adhere or rebound, scatter or flow off. Whether the droplet adheres or not depends on several factors. Important factors are the chemistry of the surface, in other words the hydrophobicity, the angle the plant leaf leans with, the impact speed and the size of the droplets (Forster 2001). The time scale for the deposition is 10-1000 ms and it depends on the retraction speed of the expanded droplets on the surface. When the pesticide solution has adhered on the plant leaves, the pesticide usually needs to penetrate into the leaf in order to have any effect. The pesticide can penetrate through the lipophilic (Buchholz 2006) or the aqueous (Schönherr 2006) pathway depending on the molecular properties, i.e. the hydrophobicity. A summary of the spraying scenario can be seen in table 1. Translocation, which is the last step, is the ability for the active ingredient to reach its site of action from its point of uptake.

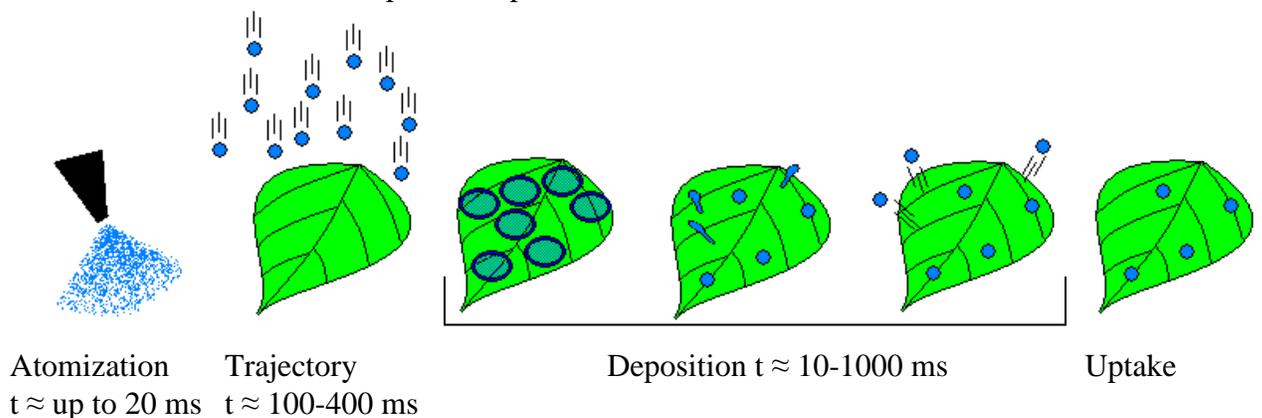


Figure 1. A schematic illustration of crop spraying.

During each of the steps of crop spraying; trajectory, deposition, uptake and translocation, there are losses, see table 1. One step where there are big losses is in the deposition step, i.e. the step where it is determined whether the droplets adhere or not. If the efficacy could be improved in this step it would have a large impact on the system efficacy.

Table 1. The system efficiency of the different steps during crop spraying. (Zabkiewicz 2007)

Spray efficacy processes	Process efficiency (%)	System efficiency (%)	Off target component (%)
Drift ^a	80-95	80-95	20-5
Deposition ^b	10-100	8-95	92-5
Uptake ^c	30-80	2.4-76	97.6-24
Translocation ^d	10-50	0.24-38	99.6-62

^aAmount deposited within target area.

^bAmount captured by plant.

^cAmount of retained material taken up into plant foliage.

^dAmount of absorbed material translocated from absorption site.

Traditionally surfactants have been used as deposition adjuvants, since they lower the surface tension of the solution. A lower surface tension leads to a lower driving force of the droplet to retract, which leads to better deposition, and also results in a better penetration of the pesticide through the hydrophobic layer of the plant leaf. The droplet size is lowered by the lowered surface tension and smaller droplets adhere better, resulting in an increased deposition. However the lower droplet size also increases the drift problem. There is obviously an optimum in the droplet size when it comes to the system efficacy. Some companies produce polymeric adjuvants, often called “stickers”, which are used as deposition enhancing additives. Examples are hydroxypropylated Guar Gum, polyethylene glycol, polyacrylic acid and polyacrylic acid latex.

Polymers

Cellulose

Cellulose is the most abundant biopolymer on earth and it is found in terrestrial plants (Westbye 2008). Cellulose is a polysaccharide consisting of six-member rings, called anhydroglucose units, see figure 2. Native cellulose forms crystalline structures due to its tendency to form intra and inter molecular hydrogen bonds (Westbye 2008), which makes it insoluble in water (Karlson 2002).

By modifying the structure, i.e. interrupting the hydrogen bond network, water soluble cellulose can be produced. One way is to introduce hydroxyethyl groups, CH₂-CH₂-OH, and/or ethyl groups, CH₂-CH₃, to the cellulose which results in an irregular structure of cellulose which prevents a crystalline structure to form. Each anhydroglucose unit has three hydroxide groups which are available for modification. When a hydroxyethyl group is reacted to a hydroxide group, the new end group presents a new hydroxide group that is also available for reaction. In this way several hydroxyethyl groups may form short side chains. On the other hand if an ethyl group is added, no new hydroxide group is formed and thereby no more groups can be added at that spot, thus only one ethyl group is possible at each side chain. Ethyl hydroxyethyl cellulose, EHEC, contains both ethyl and hydroxyethyl groups while

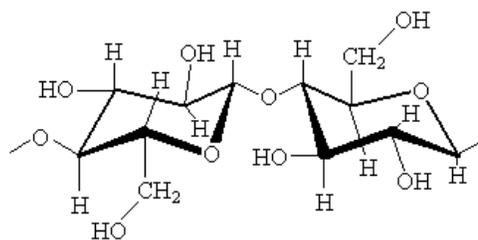


Figure 2. The repeating unit, i.e. the monomer, of cellulose. The repeating unit is called cellobiose and consists of two anhydroglucose units.

hydroxyethyl cellulose, HEC, only contains hydroxyethyl groups, see figure 3. The average number of hydroxyethyl groups that has been added onto each anhydroglucose unit is denoted as the molar substitution, MS_{EO} . The average number of ethyl groups added to each anhydroglucose unit is denoted as the degree of substitution, DS_{ethyl} .

The HEC/EHEC can be modified with hydrophobic side groups, which strongly impacts its solution properties (Karlson 2002). The hydrophobic side groups, of the polymers studied in this thesis, are alkyl groups with a length of 12 – 16 carbons.

The EHEC's and HEC's are considered to have a flexible backbone.

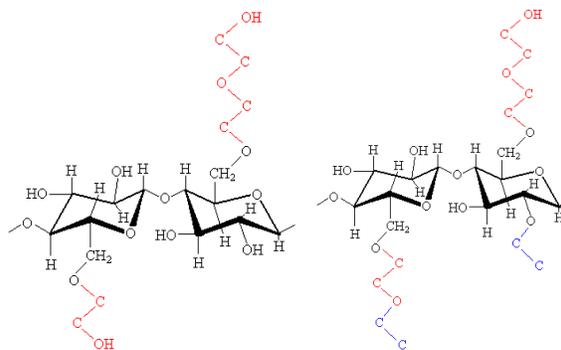


Figure 3. Schematic picture of HEC, to the left, and EHEC, to the right.

Controlling droplet size and deposition

Rheology

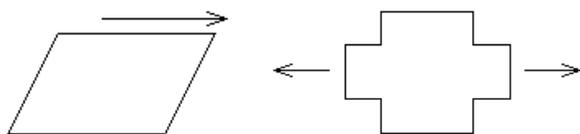


Figure 4. A Schematic illustration of the difference between shear viscosity, to the left, and elongational viscosity, to the right.

Shear viscosity, often called solely viscosity, is the measure of the resistance that a material demonstrates during shearing. Newtonian fluids are liquids that show shear viscosity proportional to the applied stress. Non-Newtonian fluids, like

polymer solutions, can be shear thinning, i.e. pseudoplastic, which means that the viscosity decreases with increasing shear rate. In the case of a polymer solution, this is due to alignment of the polymers in the direction of the applied shear.

The elongational viscosity is a measure of the resistance that a material demonstrates when it's being elongated, e.g. when a droplet is hitting a plant leaf and is expanding on its surface. The difference between the shear viscosity and the elongational viscosity is shown in figure 4. A reason why some polymers show improved droplet adhesion is due to their high elongational viscosity (Bergeron et al. 2000). When a polymer solution is being elongated or retracted, the polymer chains are being unfolded/deformed and this drains energy from the droplet (Smith and Chu 1998), which poses as a resistance in the liquid, thus reducing the risk of rebounding or scattering. The elongation phenomena is highly interlinked to the polymer conformation; polymers that are flexible and expandable as Polyacrylamide show a more pronounced elongational viscosity compared to a rigid polymer as Xanthan Gum, a semirigid polymer as Carboxymethyl Cellulose and a flexible, but compact polymer as Polyisobutylene, see figure 5 (Ng et al. 1996). Polymers that show high elongational viscosity usually have a high molecular weight (Bergeron 2003; Zabkiewicz 2007).

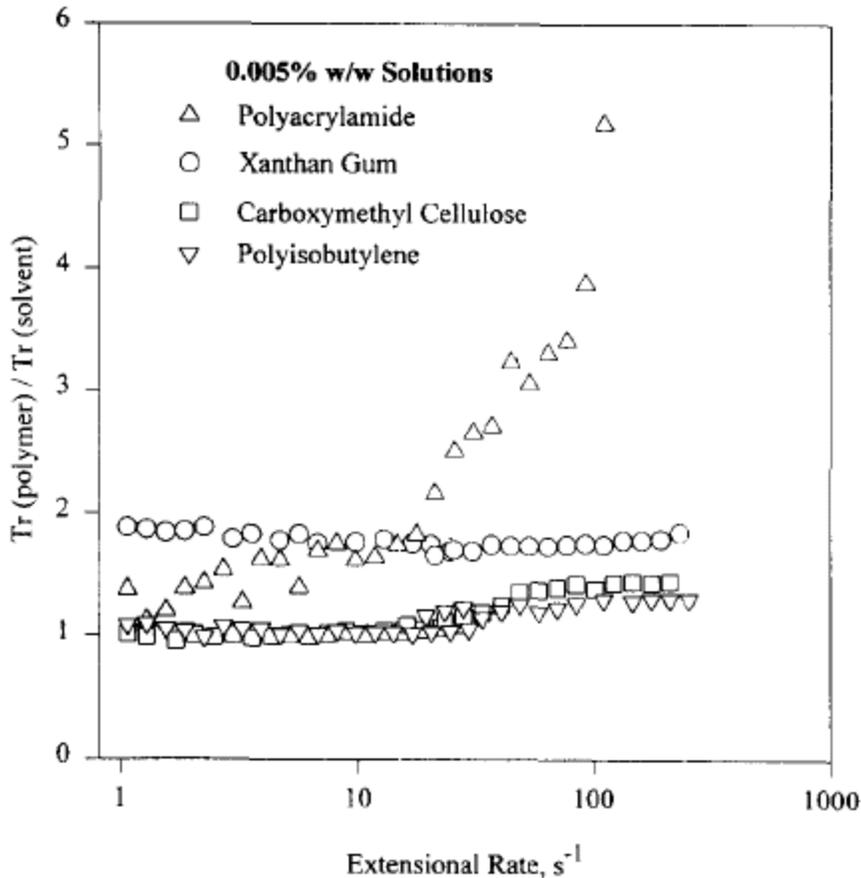


Figure 5. Shows how elongational viscosity depends on the elongational rate. (Ng et al. 1996). On the Y-axis is the value of the elongational viscosity of the polymer in a solvent divided by the elongational viscosity of the pure solvent. A value of 1 means that the polymer doesn't increase the elongational viscosity at all, while a value of 2 means that the elongational viscosity is doubled when the polymer is added. The polymer concentration is 50 ppm.

Elongational viscosity, just like shear viscosity, can depend on the elongational/shear rate and be e.g. shear thinning (Dexter 1996), this phenomena can be seen in figure 5. When it comes to flexible polymers, there is usually a drastic increase in the elongational viscosity beginning at a certain elongational rate. This is when the elongational rate is enough to deform the polymer chains (Ng et al. 1996).

All solutions show elongational viscosity. For a Newtonian fluid the elongational viscosity is exactly three times the shear viscosity (Bergeron 2003). For non-Newtonian fluids, like the tested polymer solutions, the elongational viscosity can exceed the shear viscosity by several orders of magnitude (Bergeron 2003).

Elongational viscosity has been shown to increase the average droplet size and narrowing the droplet size distribution during atomization in the spray nozzle (Bergeron 2003; Mun et al. 1999; Ergungor et al. 2006). The increase in average droplet size is important since small droplets are more prone to drift and thus hit off target (Bergeron

2003). However if the droplet size is increased the probability of rebound/scatter is increased (Zabkiewicz 2007).

There are several methods to measure the elongational viscosity. One instrument that measures the elongational viscosity is called Rheometrics RFX Fluids analyzer. It uses two opposing jets to create an area of extensional flow (Kennedy et al. 1995). Another technique is called CaBER, capillary break-up elongational rheometry. A liquid bridge of the fluid is formed between two cylindrically shaped fixtures. The upper fixture is then quickly moved upwards and stops at a certain distance, resulting in an elongated liquid thread. The evolution of the thickness of the necking is monitored (Rodd et al. 2005).

Dynamic surface tension

Surfactants are, just like polymers with high elongational viscosity, influencing the droplet size during spraying through a nozzle (Bergeron 2003) and this is due to the lowering of the surface tension. Addition of surfactants into an aqueous solution reduces the droplet size. Also surfactants that reduce surface tension quickly have the ability to enhance deposition by lowering the surface tension on the same time scale as the droplets are extended upon impact to the hydrophobic surface (Bergeron 2003). If polymers and surfactants coexist in the same solution they will interact and this gives effects on the rheology of the system, this interaction is explained in the following chapter.

Polymers and surfactants

When polymers are added to a solution the viscosity increases. At low concentrations the polymers are separated from each other and don't interact; the increase in viscosity is low. At higher concentrations the polymers in the solution will start to interact with each other. If more polymers are added from this point on the viscosity will increase much faster. The concentration where the polymers start to interact is called the overlap concentration. This overlap concentration is dependent on the molecular weight of the polymers (Karlson 2002) and hydrophobic interactions.

When surfactants are added to a solution the surface tension is lowered. This is due to the structure of the surfactant that contains a hydrophilic, water loving, and a hydrophobic, water hating, part. The hydrophilic part wants to be surrounded by water while the hydrophobic part wants to get away from it. One way to achieve this is to have the surfactant at the surface of the water, thus letting the hydrophilic part be in water while the hydrophobic part is surrounded by air.

A water molecule in the bulk is surrounded by other water molecules, while a molecule at the surface is surrounded by fewer water molecules and some air. Water experiences favorable interactions when in the bulk, while at the surface it has to interact with air, which isn't nearly as favorable. This results in the water to try to minimize the number of interactions with air and this is done by minimizing the surface area by forming a spherical droplet. Since surface active molecules, like surfactants, consist of one part that wants to interact with water and one part that rather interacts with air, there will be an accumulation of surface active molecules at the surface of the droplet. Since these molecules exchange water molecules at the surface, the number of unfavorable interactions between water and air is lowered. The more surfactant that is added, the lower is the amount of water present at the surface and this lowers the driving force of the

water to minimize the surface area. Surfactants act similarly when coming into contact with hydrophobic surfaces; the surfactants accumulate at that interface just like in the case of air.

The studied polymers are surface active, similar to surfactants. The difference is the dynamics of them. The surfactants are small and thus moves around more quickly than most polymers, which are considerable larger. There are two types of surface tension, the dynamic and the static surface tension. The dynamic surface tension is the ability to reach and fill the surfaces of newly formed surfaces with surface active molecules, in a short period of time, while the static surface tension isn't time dependent i.e. the surface tension reach equilibrium,. During e.g. atomization in a spray nozzle or when a droplet impacts on a surface, the dynamic surface tension is important since the course of events happen in a very short time scale. When e.g. a droplet sits on a plant leaf it is the static surface tension that is important and one of the deciding factors whether the droplet will flow off or not.

If the concentration of surface active molecules is high, the molecules will find new ways to hide their hydrophobic parts from the water. Surfactants do this by joining together and forming spherical micelles. The surfactants point their hydrophilic part towards the surface of the micelles to let it interact with water while the hydrophobic parts are hidden inside the micelle where there is no water. The concentration when micelles start to form is called the critical micelle concentration, CMC. Polymers are too large and bulky to form spherical structures. If the polymers have hydrophobic side groups they will interact by pushing their hydrophobic parts together, thus lowering the amount of water that surrounds them. This results in the formation of a weak network between the polymers which results in an increased shear viscosity of the solution. If a solution contains both surfactants and polymers with hydrophobic side groups there will be an interaction between them, illustrated in figure 6. At low concentration of surfactants they will all go to the surface between water and air and lower the surface tension. At a higher concentration the surfactants will start to go to the hydrophobic parts of the polymers and begin to cover them, the concentration where this happens is called the critical association concentration, CAC (Holmberg et al. 2007). This interaction works like a glue and reinforces the interactions between the polymer chains, which is represented by an increase in viscosity (Holmberg et al. 2007). At higher concentrations the surfactants start to form micelles around the polymers hydrophobic parts and the interaction between the polymers get even stronger. When the concentration of surfactant is just enough to cover all the hydrophobic polymer parts with micelles the viscosity reaches a maximum. Addition of more surfactants at this point will result in the interactions between the polymers to unfold in order to make room for more surfactants, which results in a loss of viscosity (Holmberg et al. 2007). At a certain concentration all interactions between the polymer chains are lost and the viscosity of the solution is lowered substantially. If even more surfactants are added at this point they will go to the surface, the surface tension of the solution will be lowered until CMC is reached whereby all addition of surfactants will form micelles (Holmberg et al. 2007).

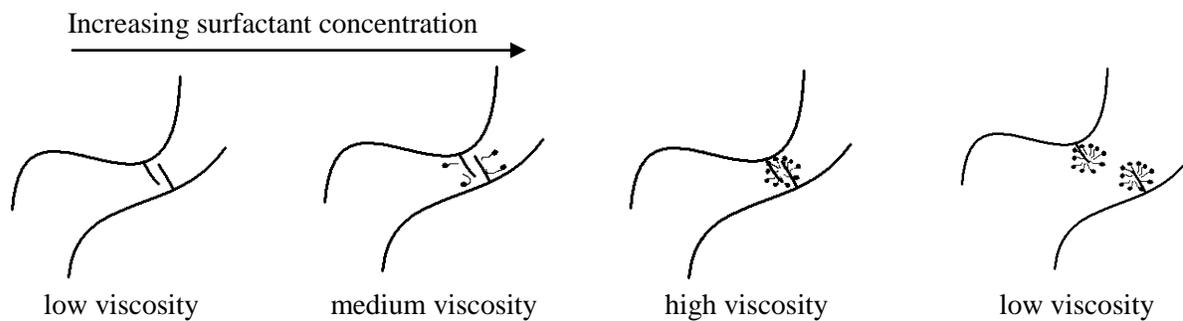


Figure 6. Schematic illustration of the interactions between surfactants and polymers with hydrophobic side groups. (Holmberg et al.2007)

Interactions between polymers and surfactants have also been shown to be able to increase the elongational viscosity of solutions (Ergungor et al. 2006).

Materials and Methods

Materials

The polymers used in this study are based on a preliminary screening of some AkzoNobel polymers. The concentrations that have been shown to be interesting for the application are between 0.02 % and 0.2 %. A few polymers from a competitor have also been studied as well as a cationic polymer. When concentrations are given in percent, it is the weight percent that is intended. All polymers are dissolved in de-ionized water.

All EHEC' except EHEC LM have hydrophobic side groups. The difference between the EHEC's is among other things different molecular weight and hydrophobic chain length, see table 2. Two HEC's are tested, one has hydrophobic side groups and one doesn't. The cationic polymer is different from the others; it is ionic and it contains surfactant. The structure of ionic polymers is stiff due to charge repulsion between the ionic groups (Karlson 2002). The structure of the EHEC's and HEC's however is much more flexible. The tested EHEC's are used e.g. as thickening agents and dispersing agents and their main usage are within the paint industry. The EHEC's belong to Cellulosic Specialties, which is a part of AkzoNobel Functional Chemicals. The tested HEC's, produced by Ashland/Aqualon, are competitors to the EHEC's, and the cationic polymer belongs to AkzoNobel.

Table 2. *The characteristics of the tested polymers.*

Polymer name	Type	DS _{ethyl}	MS _{EO}	(w/w) % hydrophobe	Hydrophobe length	Molecular weight (kDa)
HEC LM	HEC	0	2.5	0	-	250
HM-HEC LM	HEC	0	2.5	1	C16	250
EHEC LM	EHEC	1	2	0	-	250
HM-EHEC LM	EHEC	1	2.5	1	C14	250
HM-EHEC MM	EHEC	1	2.5	1	C12-C14	500
HM-EHEC HM	EHEC	1	2.5	1	C12-C14	1000
Cationic polymer	cationic polymer					-

Static surface tension

Static surface tension is measured on a KSV Sigma70, from KSV instruments, using the du Noüy method. A platinum ring is lowered into the solution and then lifted slowly. The force needed to raise the ring from the solution is measured. There will be a maximum force during the lifting sequence and this force is used to calculate the surface tension of the solution. The surface tension is calculated using equation 1,

$$\gamma = \frac{\beta \cdot F}{4\pi \cdot R} \quad (1)$$

where γ is the surface tension, F is the pulling force, R is the radius of the ring and β is a correction factor. Polymer solutions with a concentration of 0.1 % are tested.

Dynamic surface tension

The dynamic surface tension is measured with a maximum bubble pressure instrument, PC500-L Surface Tensiometer, from Sensa Dyne. The instrument is generating bubbles in the solution. The faster the bubbles form, the faster dynamic surface tension is measured. Different speeds to generate the bubbles are used in order to see how the surface tension depends on the time scale. Polymer solutions with a concentration of 0.1 % are tested.

Rheology

The rheology data is measured with an AR-G2 rheometer from TA Instruments. A 0.5° cone with a diameter of 60 mm and a truncation of $17\ \mu\text{m}$ and a 1° cone with a diameter of 60 mm and a truncation of $26\ \mu\text{m}$ are used for the measurements. The sample is applied on a stationary plate and the cone is lowered to the geometry gap. A force is applied to the sample through the cone. The force can be applied in two different ways; through a rotating movement or through an oscillating movement. There are several different modes available that allows the measure of different properties of the material. By using a rotating movement and continuously increasing the shear rate you get information about whether the material shows a Newtonian, a shear thinning or a shear thickening behavior. With an oscillating movement and continuously increasing the frequency you get information about the viscous and the elastic modulus, G'' and G' , at different time scales. There are also possibilities to e.g. measure the creep and the recovery of the material. Polymer solutions with concentrations of 0.1 %, 0.2 %, 0.5 % and 1 % are tested.

Drop test – tilting plane

The experimental setup for the drop test is shown in figure 7. A syringe is used to drip droplets onto a surface. The surface is covered with parafilm to represent a very hydrophobic plant leaf. The surface is turnable and with the help of a protractor the current angle is easily determined. A syringe is placed 50 cm above the surface, just above the center of the turning axis. The speed of the droplet at impact is 3.1 m/s. A series of five droplets are dripped onto the surface. If the majority of the droplets adhere to the surface without flowing off, rebounding or scattering the solution is considered to adhere at the current angle. The maximum angle where adhesion occurs is determined. The drop test is intended as a screening method to evaluate different polymer solutions when it comes to their deposition properties. Polymer solutions with concentrations of 0.02 %, 0.04 %, 0.1 % and 0.2 % are tested.

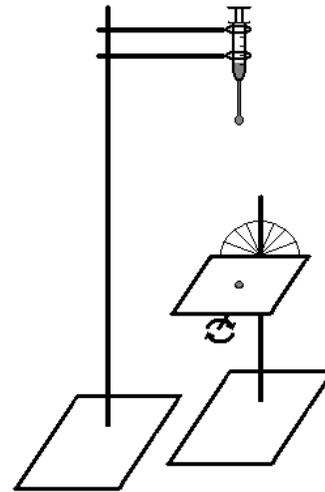


Figure 7. A schematic illustration of the experimental setup for the drop test.

Drop test – droplet retraction

The experimental setup is shown in figure 8. A syringe is used to form droplets that fall onto a surface, covered with parafilm. All equipment is fixed to make sure the droplet hits the same spot each time. The droplet falling distance is set to 50 cm, resulting in a speed of 3.1 m/s at droplet impact. A high speed camera, Casio EX-FC100, allows the capture of 1 000 frames per second. A ruler is placed within the camera view as a reference. A microscope lamp is used to give good lighting with non-flickering light. The evolution of the droplet during the retraction is monitored, using the software Avidemux 2.5, where the diameter of the droplet on the surface is followed with time. The method is adopted from experiments performed by Bergeron et al. (Bergeron et al. 2000). Polymer solutions with concentrations of 0.02 %, 0.04 %, 0.1 % and 0.2 % are tested.

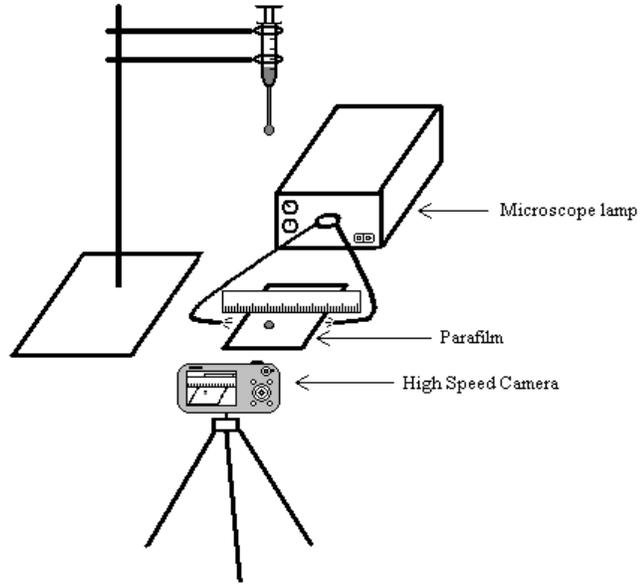


Figure 8. A schematic illustration of the experimental setup for the drop test.

Worthington jet

The experimental setup is shown in figure 9. A glass marble is released from a fixed height and hits the surface of the solution. When the sphere hits the liquid its surface gets deformed. The surrounding liquid rushes from all directions to even out the surface but when the flowing liquid meets in the middle of the crater its kinetic energy results in a splash. In the middle of the previous crater a pillar of water, also called a Worthington jet, is formed. In this experiment the height of this jet is of interest. In the experiment a glass marble is used with a diameter of 15 mm and a mass of 5 g. The size of the container must not be too small since effects from the edge or the bottom could interfere with the results. The influence of these effects has been studied by Cheny and Walters (Cheny and Walters 1996). It is of importance to have a smooth and dry surface of the glass marble since this is affecting the nature of the created jet (Cheny

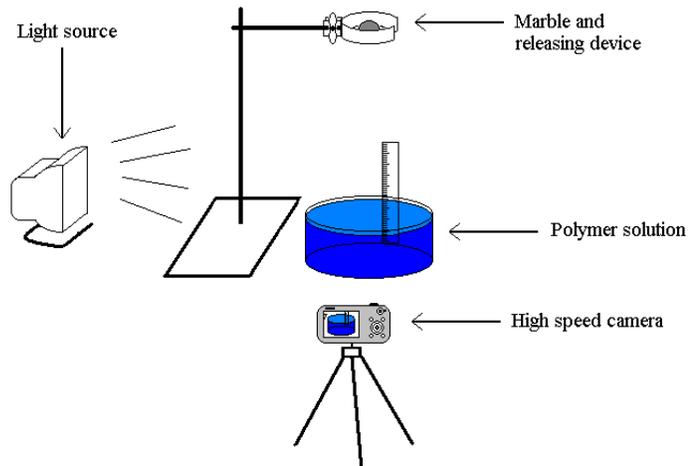


Figure 9. A schematic illustration of the experimental setup for the Worthington jet experiment.

and Walters 1999). The container that is used is made out of glass and has a depth of 9 cm and a diameter of 19 cm. The jet is studied with a high speed camera, Casio EX-FC100, that allows the capture of 1 000 frames per second. The software Avidemux 2.5 is used to study the height of the jets. A ruler is placed within the camera view as a reference. The idea for the Worthington jet experiment comes from Cheny and Walters who have done similar experiments (Cheny and Walters 1996; Cheny and Walters 1999). Polymer solutions with a concentration of 0.1 % are used.

Droplet mass

A series of 20 droplets are dripped, with a syringe, onto a balance and an average droplet mass is calculated.

Results and discussion

Rheology

HM-EHEC LM and EHEC LM are tested with a rheometer. A viscosity versus shear rate measurement is made, in order to get an indication whether the solutions are shear thinning or not. The shear viscosity is measured while the shear rate is increased continuously. This test is important when it comes to the spraying of the pesticide solution, since a low viscosity is needed. There is no evident difference in the behavior of the two polymers, when the concentration is 0.1 %, see figure 10. The instrument, with the chosen set of experimental parameters, has problems measuring below a shear rate of 10 s^{-1} . The viscosity is constant at a value of $1.6 \text{ mPa}\cdot\text{s}$, independently on the shear rate. In comparison, water has a viscosity of $1 \text{ mPa}\cdot\text{s}$. When the concentration is increased to 1 % the viscosity increases. The viscosity for EHEC LM increases about an order of magnitude, while it increases almost three orders of magnitude for HM-EHEC LM. EHEC LM are slightly shear thinning at high shear rates, while HM-EHEC LM shows a pronounced shear thinning behavior that starts at a much lower shear rate. When the shear rate is increased the difference in viscosity between the two polymers gets smaller, finally converging at high shear rates.

The 0.1 % solutions behave the same and that is most likely because there are very few intermolecular interactions between the polymer chains in the solutions, indicating that the concentration is below the overlap concentration. At a concentration of 1 %, difference between HM-EHEC LM and EHEC LM is seen and this is because the polymers interact to a much larger extent, which means that the concentration most certainly is higher than the overlap concentration. HM-EHEC LM has a higher shear viscosity than EHEC LM and that is due to the fact that HM-EHEC LM has hydrophobic side groups, which increase the intermolecular interactions between the polymers in the solution. When the shear rate is increased, the interactions break. Without interactions, the difference between the two polymers must be very small, just as in the case of the 0.1 % solutions. This is the reason for the shear thinning behavior. The shear rate when spraying is between $1\,000 \text{ s}^{-1}$ and $10\,000 \text{ s}^{-1}$ (Mezger 2006) and at these shear rates the viscosity is very low for the 0.1 % samples, thus it should most certainly be no problem spraying these solutions.

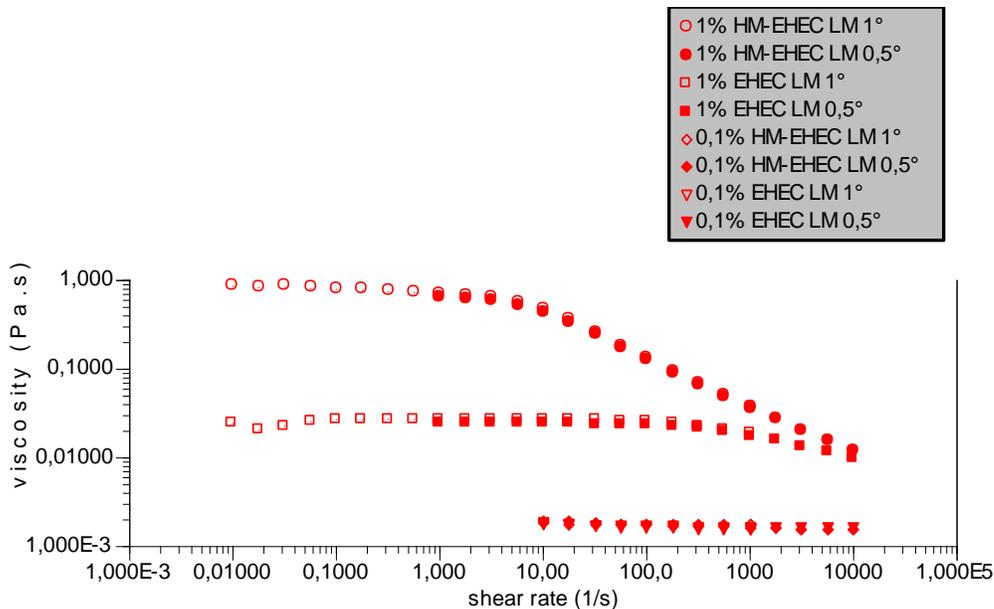


Figure 10. A flow curve of HM-EHEC LM and EHEC LM at two different concentrations. To be able to measure the wide shear rate interval, both the 0.5° and the 1° cone is used.

The same polymers are tested using a frequency sweep, in order to see how the material behavior changes with the time scale. It is interesting to see if the material becomes elastic at short time scales, since it could be a part of the explanation why the polymer solutions increases droplet deposition. Prior to this measurement a stress sweep is made in order to get a stress value that is within the linear viscoelastic region, LVER, and the frequency sweep is performed using this stress. The stress that is used is 0.5 Pa for the 0.1 % solutions and 0.3 Pa for the 1 % solutions. In the figures, the viscous modulus is represented by G'' and the elastic modulus is represented by G' . Solutions containing 0.1 % polymer show a viscous behavior with practically no elastic modulus at low frequencies, see figure 11 a. With the set of parameters used, the instrument is able to measure up to a frequency of a couple of hertz and at this point the viscous and the elastic modulus seem to converge. However since the solutions are in the diluted regime, both the viscous and the elastic modulus is very low. There is no evident difference between HM-EHEC LM and EHEC LM at this low concentration, just as in the flow curve. As already discussed, this is most likely because there are very few intermolecular interactions in the solution at this concentration.

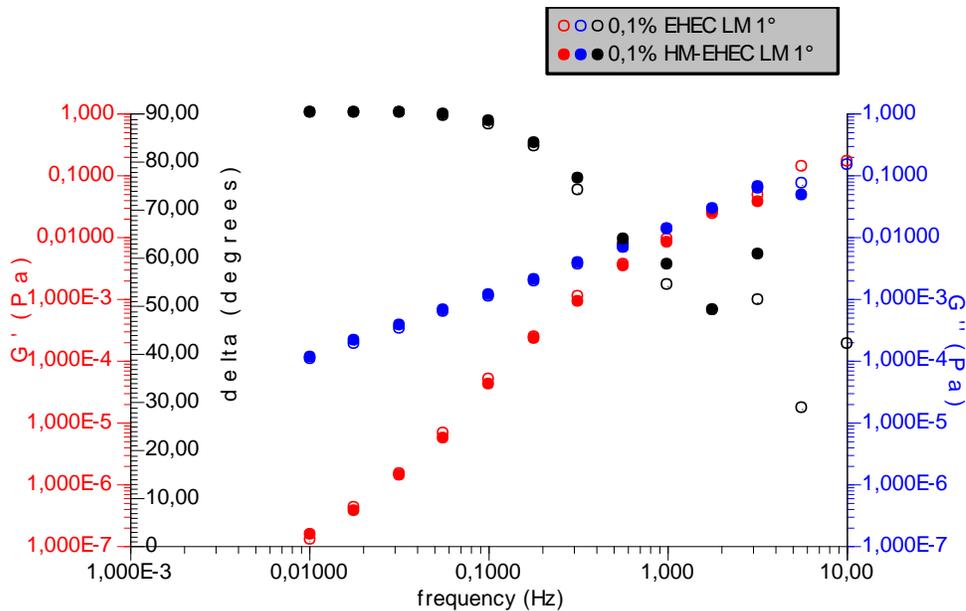


Figure 11 a. A frequency sweep of HM-EHEC LM and EHEC LM at a concentration of 0.1 %. The 1° cone is used.

When the concentration is increased to 1 % several differences are seen, see figure 11 b. The viscous modulus increases for both, but by far most for HM-EHEC LM. The elastic modulus for HM-EHEC LM increases several orders of magnitude, while EHEC LM's elastic modulus is on the same level as for the 0.1% solutions. With the 1 % solutions the instrument is able to measure up to a frequency of about five hertz and at this point the viscous and the elastic modulus seem to converge, just as in the case of the 0.1 % solutions. At the concentration of 1 % there are big differences between the polymers. As already discussed, this is most likely because there are a lot more interactions between the polymers chains in these solutions.

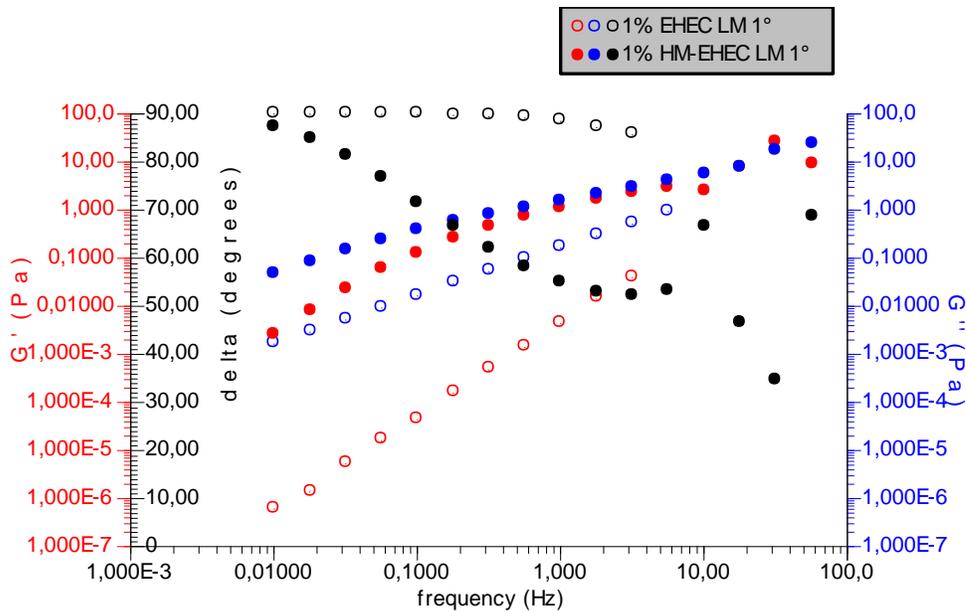


Figure 11 b. A frequency sweep of HM-EHEC LM and EHEC LM at a concentration of 1 %. The 1° cone is used.

When a droplet hits a hydrophobic surface and expands, it is exposed to a force. By using the simple formula; $F = m \cdot a$, where F is the impact force, m is the mass of the droplet and a is the acceleration, or in this case the deceleration, an approximation of the force is calculated to a value of 197 Pa. A new frequency sweep is performed, using parameters that are more realistic for the application. This calculated stress value of 197 Pa, which is outside the LVER, is applied on HM-EHEC LM and EHEC LM solutions of different concentrations using a frequency sweep, see figure 12 a and figure 12 b. The droplet impact and expansion on a hydrophobic surface happens within a few milliseconds, which would be represented by a frequency of several hundred hertz, and the idea is to see whether the sample acts more elastic or not on such a short time scale. However with the chosen set of experimental parameters the instrument is able to measure from a frequency of 4 Hz up to about 50 Hz in the best cases. It is however still interesting to see what happens with the rheology when the time scale is changed, since it could give an indication of what happens in the real case.

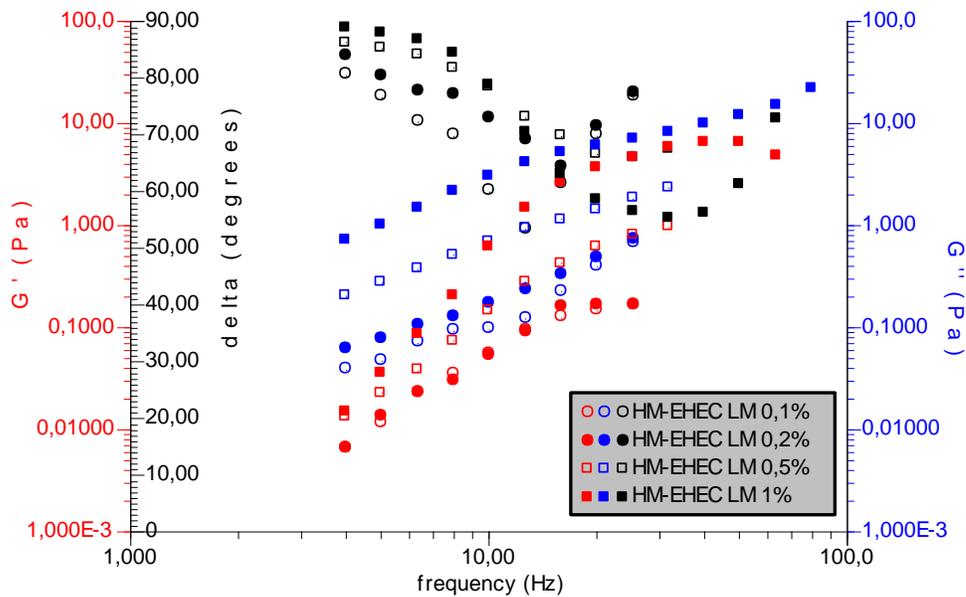


Figure 12 a. A frequency sweep of HM-EHEC LM at four different concentrations. The 0.5° cone is used.

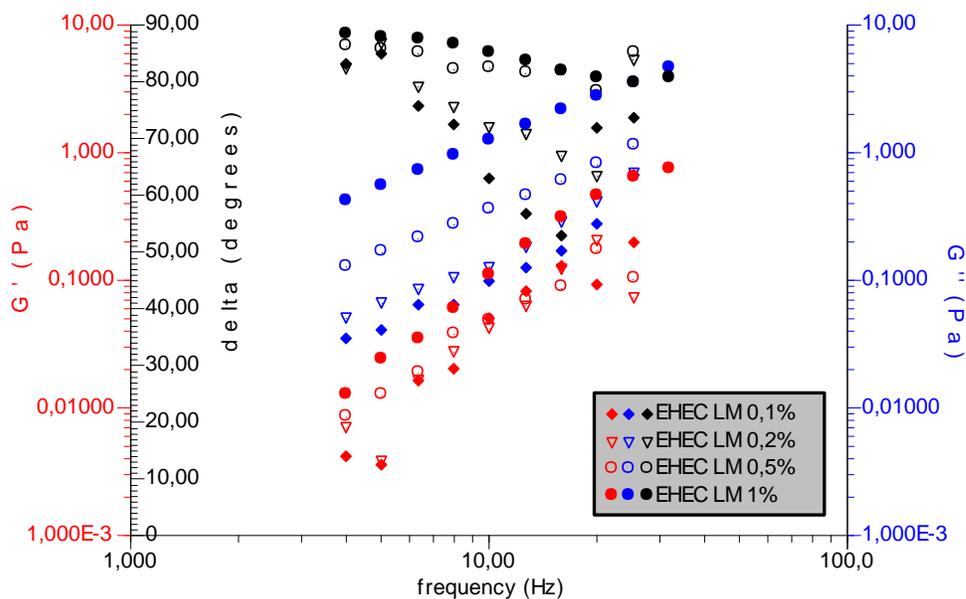


Figure 12 b. A frequency sweep of EHEC LM at four different concentrations. The 0.5° cone is used.

HM-EHEC LM and EHEC LM solutions with concentrations of 0.1%, 0.2%, 0.5% and 1% are tested. The elastic modulus of the concentrations up to 0.5% for EHEC LM and up to 0.2% for HM-EHEC LM lies on the same level, increasing some as the frequency increases. At higher concentrations the elastic modulus does increase. HM-EHEC LM, that increases its elastic contribution at lower concentration compared to EHEC LM, also show a larger increase in the elastic behavior, especially at higher

frequencies. However during the entire range of measurement the viscous contribution dominates, meaning that the elastic contribution overall is low. The viscous modulus increases as the concentration increases. HM-EHEC LM have a more pronounced increase due to its hydrophobic side groups, which increases the interactions between the polymer chains.

When the frequency increases, the elastic and the viscous contribution increase, at least during the frequency interval used in the measurements. It is however difficult, by the results from these measurements, to predict the elasticity of the solutions during the impact of droplets onto hydrophobic surfaces. This is because the instrument isn't able to measure at a high enough frequency. However what can be concluded is that HM-EHEC LM seems to have a larger elastic modulus compared to EHEC LM, at a concentration of 0.5 % or more, and this is due to the hydrophobic side groups. No evident differences are detected between the two polymers at the concentrations that are interesting for the application, 0.02 % – 0.2 % and with the experimental parameters that is used.

Droplet impact

The drop test shows that all tested polymers improve the deposition to hydrophobic surfaces, but to different extent, see figure 13. The results also show that the concentration of polymer in the solution is of big importance, a higher amount of polymer results in a more pronounced effect. However, when the concentration is increased above 0.1 %, the deposition enhancing effect seems to be small. The optimal polymer concentration thus seems to be somewhere between 0.04 % and 0.1 %.

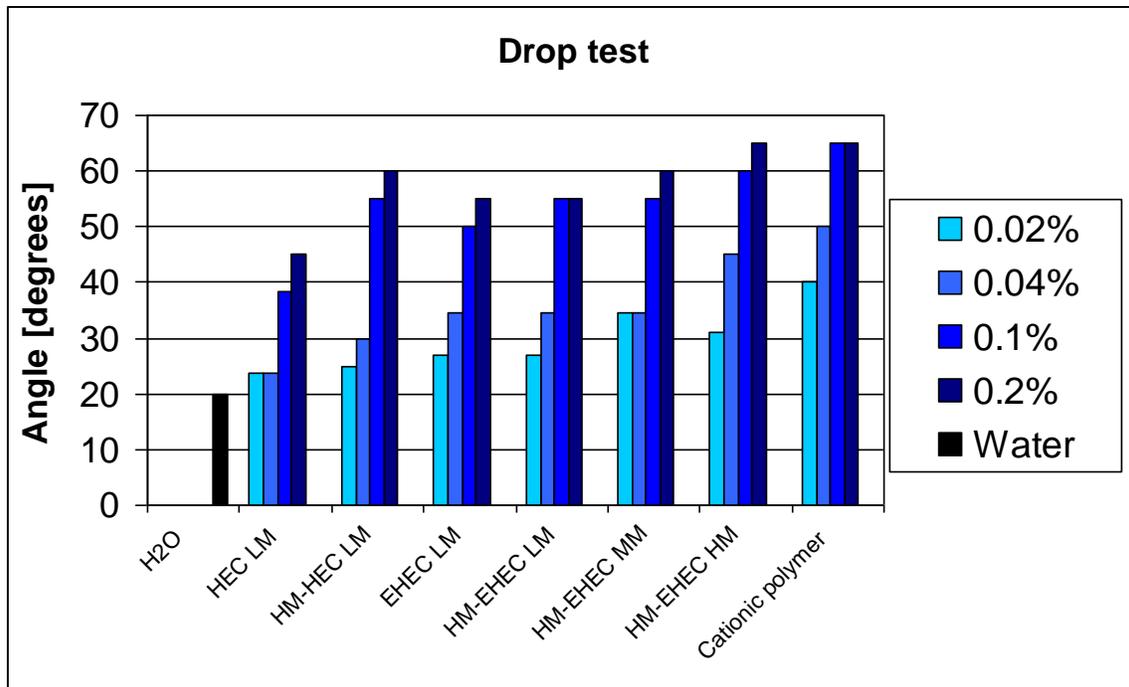


Figure 13. The result from the drop test with the tilting plane. For information about the different polymers, see table 2.

The best polymer in the test is the cationic polymer. Among the cellulose based polymers, HM-EHEC HM shows the best result while HEC LM shows the worst. HM-

EHEC HM is the polymer with the highest molecular weight, out of the ones tested, and HEC LM is a HEC without hydrophobic side groups. A trend in the results is that a higher molecular weight increases the deposition. This is no surprise since polymers that show high elongational viscosity usually have high molecular weight (Bergeron 2003; Zabkiewicz 2007).

HEC LM and EHEC LM have in contrast to the other tested cellulose based polymers, no hydrophobic side groups. EHEC LM shows almost as good results as the EHEC's with hydrophobic side groups, while HEC LM is considerably worse than HM-HEC LM, which is an HEC with hydrophobic side groups. The difference in the results between HEC LM and EHEC LM seems to come from the ethyl groups that are added to the latter polymer, since this is the main difference between them. The ethyl groups make the cellulose more hydrophobic and this will most certainly lead to more and stronger intramolecular interactions, since a more hydrophobic structure are more prone to stay away from the polar environment of the water. Stronger intramolecular interactions lead to an increased need for energy in order to extend the polymer chains, thus more energy can be dissipated during the droplet impact, leading to less energy available for rebound. The difference between HM-HEC LM and HM-EHEC LM is that the prior is a HEC while the latter is an EHEC, both having hydrophobic side groups. The result for these two polymers are more or less identical, they seem to work as good as the other. The ethyl groups thus seem to have no evident effect in this case. The most probable explanation for this is that the intramolecular interactions are changed to more or less solely interactions between the hydrophobic side groups, eliminating or at least strongly reducing the effect from the ethyl groups.

When a droplet hits a hydrophobic surface, like a parafilm, the droplet first expands whereby it starts to retract. A sample of water will in just 10 ms retract back to the diameter the droplet had before it hit the surface. This corresponds to an average velocity of almost 0.5 m/s. Due to the high kinetic energy of the droplet; it will rebound from the surface. The course of events that occur when a droplet of water hits a parafilm surface is shown in figure 14.

The average retraction speed is calculated for several different polymers at a concentration of 0.1 %. By plotting these values in a graph versus the results from the drop test with the tilting plane, a trend can be seen, see figure 15. On the X-axis is the average retraction speed of the polymer solutions over the first 100 ms; water and the

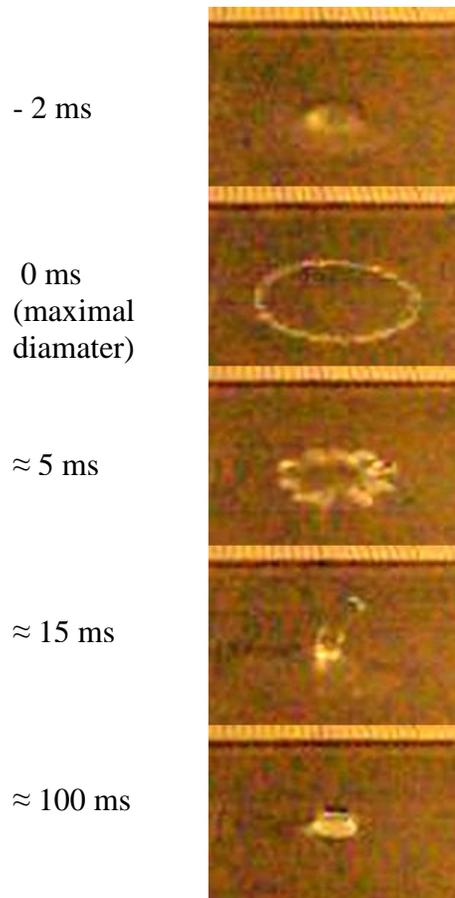


Figure 14. *The course of events that occur when a droplet of water impacts on a parafilm surface.*

cationic polymer which fully retracts before 100 ms gets a somewhat misleading value in the graph. On the Y-axis is the result from the drop test with the tilting plane, i.e. the maximum angle the polymer solutions are able to adhere to. Each point represents a unique polymer solution. The trend is clear; a low retraction speed of the droplet corresponds to a droplet that adheres well on the surface. A droplet that retracts fast corresponds to a droplet that is prone to rebound. However there is an exception, the cationic polymer, that has a high retraction speed but at the same time enhances the deposition most of all tested polymers.

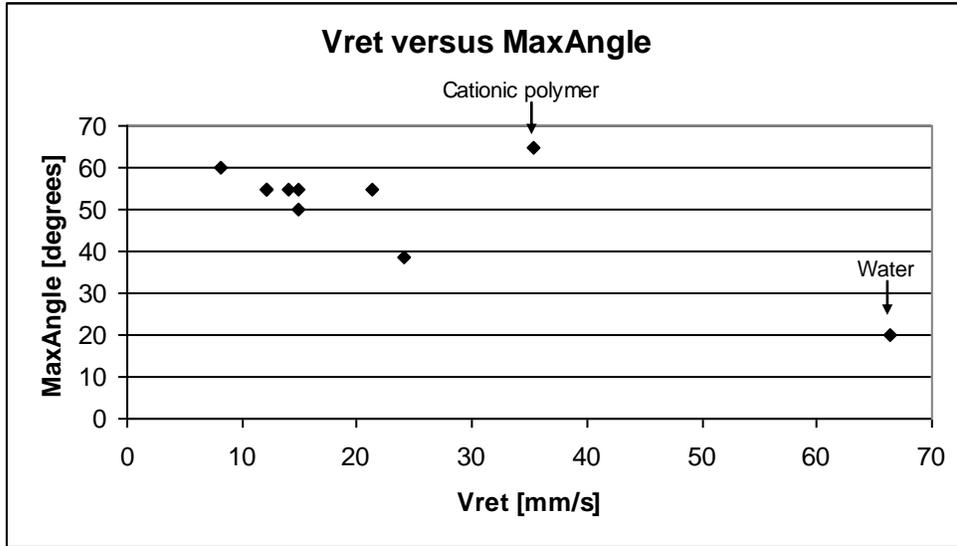


Figure 15. The correlation between the deposition effect, MaxAngle, and the droplet retraction speed, Vret, is shown.

The retraction speed of solutions with different concentrations of HM-EHEC LM and EHEC LM is measured and plotted versus the results from the drop test with the tilting plane, see figure 16. The same trend is seen, as in figure 15, droplet adhesion is correlated to the retraction speed of the droplets. Figure 16 also clearly shows that the retraction speed of the droplets is dependent on the polymer concentration; a higher concentration of polymer will lower the retraction speed of the droplets.

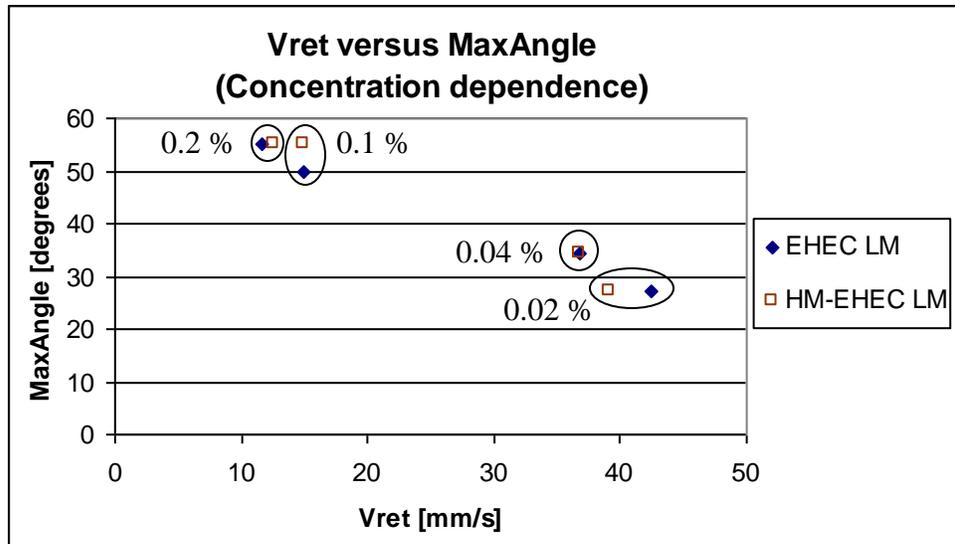


Figure 16. The concentration dependence of the droplet retraction speed and the deposition enhancing effect is shown for two polymers. The points, going from left to right, represents the concentration of 0.2 %, 0.1 %, 0.04 % and 0.02 % polymer. For explanation of MaxAngle and Vret, see figure 15.

The retraction speed of the droplets has been correlated to the elongational viscosity (Bergeron et al. 2000). This indicates that the cationic polymer has a rather low elongational viscosity, due to its high retraction speed. This suggest there is something else than the elongational viscosity that makes the solutions of the cationic polymer adhere to hydrophobic surfaces. Something is happening that make the droplets adhere instead of rebounding, this without dissipating much energy during the retraction process. Since the retraction speed is fast, while at the same time the droplet doesn't rebound easy, the majority of the dissipation of energy must occur in the end when the droplet is more or less fully retracted.

The cationic polymer is quite different from the other polymers; it is the only ionic polymer and it also contains surfactant. Something that is clearly seen if a 1 % solution of the cationic polymer is compared to the other studied polymers is that the cationic polymer solution is very viscous compared to the rest. However at the concentrations which are interesting for the application, 0.02 % - 0.2 %, the difference in viscosity is hard to distinguish; the samples all have a very low viscosity. The ionic property or the fact that there are surfactants present could explain the difference in behavior. You could think that the surfactants should lower the size of the droplets, which would lead to a better deposition result since smaller droplets are less prone to scatter, rebound and flow off. However the size of the droplets of the cationic polymer solutions is similar to the other polymer solutions and actually slightly larger than most droplets of the other polymers. The dynamic surface tension of two 0.1 % polymer solutions is measured and it shows that the cationic polymer actually has a higher value than HM-EHEC LM, which explains the larger droplet size, see figure 17. The lower the surface tension the lower is the driving force for the droplet to reduce its surface area, and this result in smaller droplets, which have a larger area to volume ratio. The ionic character of the cationic polymer might be responsible for its unexpected behavior. A polyelectrolyte,

like the cationic polymer, is rather stiff due to the charge repulsion of the ionic groups (Karlson 2002). Flexible polymers are known to have a high elongational viscosity since they are able to change their conformation during an elongational flow. The cationic polymer will not be able to do that to the same extent as the cellulose based polymers due to its structure and this is the reason why it shows a low elongational viscosity.

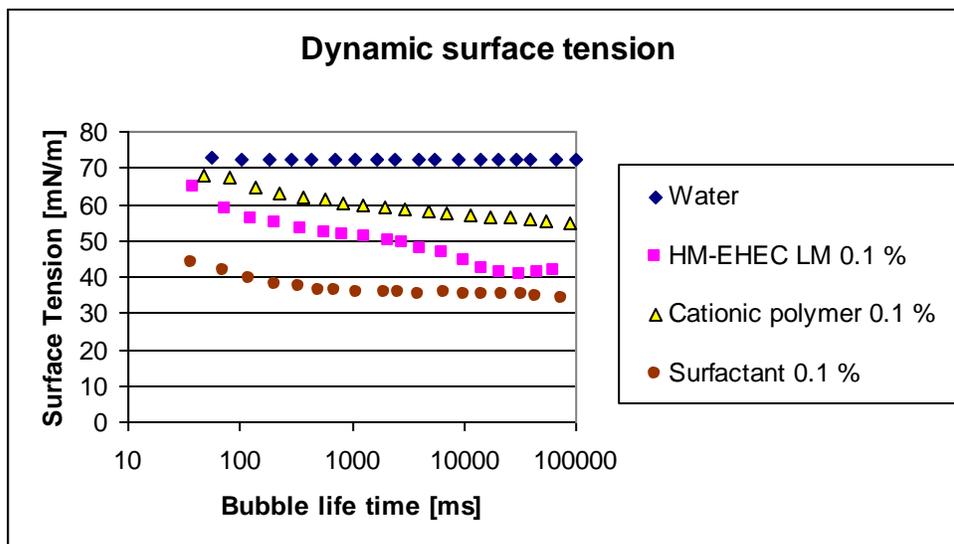


Figure 17. The surface tension as a function of the bubble life time is shown for two polymers, a currently used adjuvant and water.

As previously concluded, the retraction speed of droplets is correlated to the droplet adhesion. This has previously been studied by Bergeron et al. where they compared water with an aqueous solution containing a low concentration of polyethylene oxide, which is a very flexible polymer (Bergeron et al. 2000). They found out that if a small amount of this polymer, in this case 0.1 g/l, is added to water the droplet retraction speed is lowered. These results correlates with the results from the experiments conducted in this thesis, since the cellulose based polymers are flexible. Bergeron et al. also concluded that if the retraction speed exceeds 300 mm/s the droplets will rebound (Bergeron et al. 2000). This agrees very well with the results from the test carried out in this thesis, where all samples with a retraction speed greater than 300 mm/s actually does rebound while droplets that retract slower than 300 mm/s doesn't rebound.

Polymer and surfactant

By the addition of a surfactant, a nonionic wetter, to solutions containing different amount of polymer, the size of the droplets created by dripping from a syringe is lowered, see figure 18 a. The CMC of the pure surfactant is around 1 g/l but it is increased somewhat due to the CAC, where the interactions with the polymers bind some of the surfactants. The size of the droplets is lowered until CMC is reached, whereby the size becomes constant. The size of the droplets seem only to depend on the surfactant concentration, the polymer concentration only affect the size if there is no surfactants present. A higher concentration of surfactant results in a decrease in surface tension and this lowers the driving force of the droplets to reduce its surface area, resulting in smaller

droplets to form. When CMC is reached there will be no further decrease in the surface tension if more surfactants is added, thus the droplet size becomes constant.

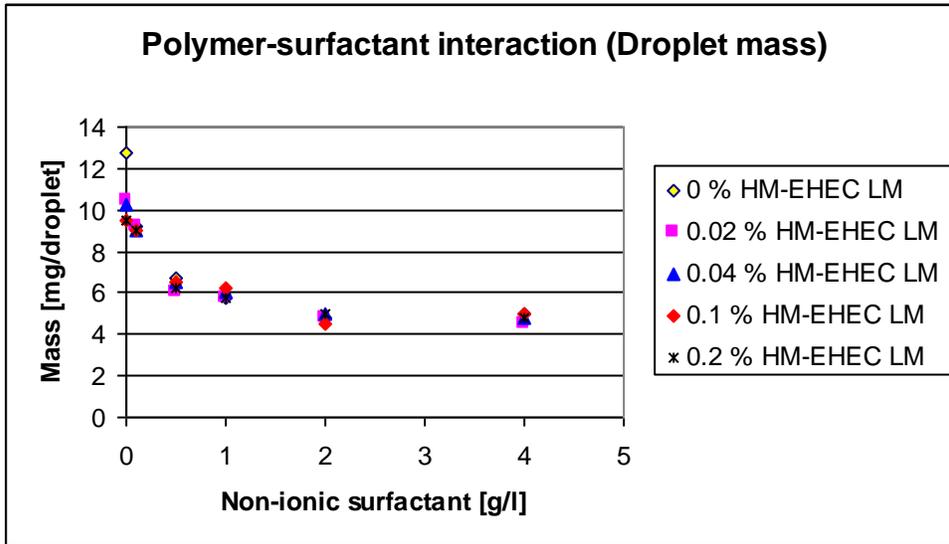


Figure 18 a. *The size of the droplets as a function of the surfactant concentration.*

The deposition effect can be improved by addition of polymer, until CMC is reached, see figure 18 b. The difference in the deposition effect is largest when there is no surfactant added and the difference gets smaller as more surfactant is added. At a concentration of 2 g/l or more the deposition enhancing effect from the polymers seems to be totally lost. When testing the solutions, using the drop test with the tilting plane, the droplets either adhere or not. The reason for not adhering could however differ between different solutions. At the angles where the droplets doesn't adhere, the droplets of the solutions with low surfactant concentration scatter, while at concentrations of 2 g/l or more the droplets solely flow off the surface. At these concentrations the droplets leave a trail of solution behind them as they flow off the surface. In these solutions, which have concentrations higher than CMC, there is a reservoir of surfactants in micelles. When the surface expands some micelles will disband in order to cover the newly created surfaces with surfactants. By having an excess of surfactants, in the micelles, the surface can expand without losing the low surface tension. If the droplet is sitting on a leaning plant leaf, the droplet expansion will occur downwards, thus the droplets are more prone to flow off a surface. The trail of solution is possible for the same reason; there are enough surfactants to cover all of the created surfaces, which make the expansion of the surface less unfavorable.

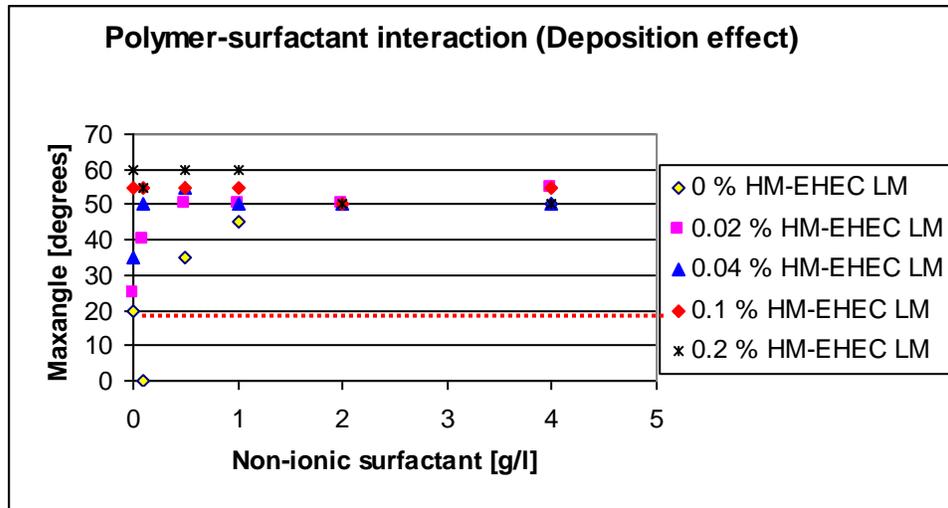


Figure 18 b. The deposition effect as a function of the surfactant concentration. The deposition value for water is indicated by the red dashed line.

The deposition seem to be more or less constant for 0.1 % and 0.2 % polymer solutions over the surfactant concentration interval of 0 g/l until 1 g/l and during this interval the weight of the droplets are lowered from around 9 mg/droplet to around 6 mg/droplet, see figure 18 a. The smaller the droplet size the more prone are the droplets to adhere, but this improvement isn't seen when decreasing the droplet size with surfactant, if the concentration of polymer is 0,1 % or more. This indicates that the surfactants are disturbing the polymers in preventing droplet rebound/scattering. The main reason for the polymers to improve the deposition is the elongational viscosity, the dissipation of kinetic energy due to the elongation and contraction of polymer molecules. This suggests that the surfactants impact this behavior in some way, reducing the elongational viscosity of the solution.

At present AkzoNobel merchandise the tested surfactant as a pesticide adjuvant that is diluted into a final usage concentration of 1 g/l. At this concentration an addition of polymers will increase the deposition effect, as can be seen in figure 18 b. Another way is to use a lower concentration of surfactant to achieve a larger droplet size, but with the help of polymers still have the same deposition effect. This would lead to less drift at the same time as the deposition effect stays at the same level.

By adding polymers the amount of pesticide solution that ends up on the plant leaves increases, thus reducing the amount of unused pesticide that is left in the ecosystem. Since a larger portion of the pesticide will end up on the leaves, the concentration of pesticide in the solution can be lowered. This leads to even lower amounts of pesticide that reaches the ecosystem. In addition to a more environmentally friendly product, a lower amount of pesticide is an economical gain as well.

The size of the droplets of different polymer solutions is measured and it shows that it differs slightly. The dynamic surface tension of two polymers is tested and compared to the tested surfactant, see figure 17 in the previous chapter. The cationic polymer and HM-EHEC LM is tested and both lower the dynamic surface tension somewhat, but the surfactant lowers the dynamic surface tension considerably more,

especially at short time scales. It is a result of the difference in the dynamics of the surfactant and the polymers. The surfactant is much faster and is able to reach the newly formed surfaces a lot faster than the large and bulky polymers. However the fact that the polymers lower the dynamic surface tension of the solutions leads to a reduced size of the droplets, just like in the case of added surfactant. The difference in droplet size between different polymer solutions however isn't large and the influence it has on the results should be very limited.

The time scale for spraying/atomization is up to 20 ms, and as can be seen in figure 17, the surfactant does lower the surface tension at that time scale. This is the reason for the lowering of the droplet size when using surfactants. The surfactant is also able to lower the surface tension in the same time scale as the retraction of droplets on hydrophobic surfaces occur, and due to this it will increase the deposition even more. This is because a lower surface tension leads to a lower driving force for the droplet to retract. When polymers are used the time scale for the retraction of droplets are increased to several hundred milliseconds, which increases the time the surface active molecules in the solution have to reduce the surface tension. As can be seen in figure 17, the polymers are able to lower the surface tension in that time scale which indicates that the polymers surface active properties most certainly enhances the deposition along with the elongational viscosity. The static surface tension of the EHEC's with hydrophobic side groups lowers the static surface tension more than the one without, see figure 19. It should be reasonable to assume that the dynamic surface tension is lower for the EHEC's with hydrophobic side groups at any time scale. It would result in the EHEC's with hydrophobic side groups to gain a larger deposition effect from the lowered dynamic surface tension compared to the EHEC without hydrophobic side groups. It is however hard to draw any quantitative conclusions of the importance of the dynamic surface tension, when it comes to droplet deposition.

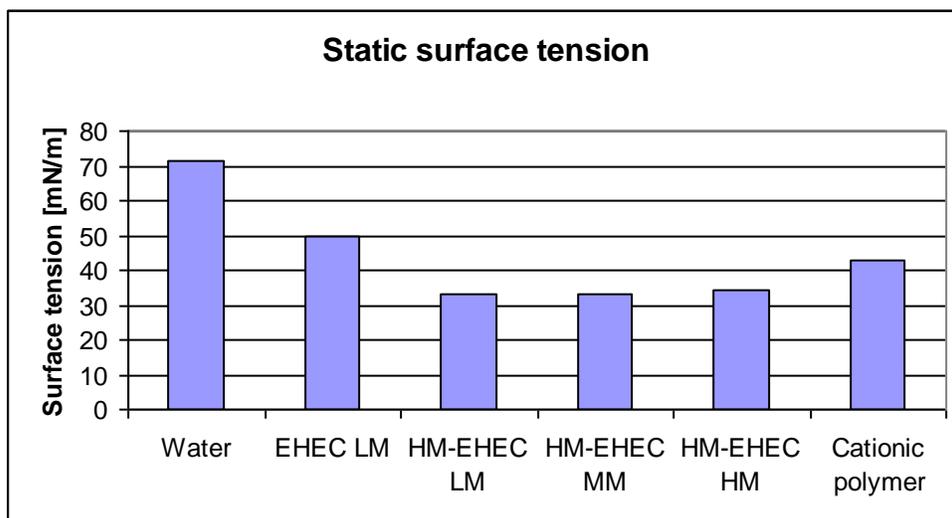


Figure 19. The static surface tension for the EHEC's, the cationic polymer and for water.

Worthington jet

The Worthington jet experiment is supposed to give similar results like the drop test where the retraction speed of the droplets is calculated. When the jet is formed the liquid is exposed to an elongational flow. The course of events that happen during the experiment is shown in figure 20. The idea is that a Newtonian liquid would result in a fairly long jet while a liquid with high elongational viscosity, like a polymer solution, would result in a shorter jet. By comparing the height of the jets of different liquids it would be possible to determine which liquids have high respectively low elongational viscosity. However the experiment isn't successful due to several reasons. First of all the jets aren't continuous, but brake up and so called satellite drops are formed at the top of the jets. Cheny and Walters have tested at which shear viscosities the satellite drops form and found out that the viscosity has to be rather high to completely get rid of the satellite drop problem (Cheny and Walters 1999). The dilute solutions tested in this thesis have low shear viscosity and are thus predicted by their results to form satellite drops and they do. However the problem is more severe than expected. The satellite drops make the comparison between different solutions difficult, especially since the extent of the satellite drop problem is different for different solutions. To be able to compare the elongational viscosity of the solutions they would have to have high enough shear viscosity for no satellite drops to form and preferable all solutions should have the same shear viscosity. The shear viscosity can be adjusted by additives, but this vastly increases the extent of the experiment and due to the short period of time available for this study the experiment had to be put aside.

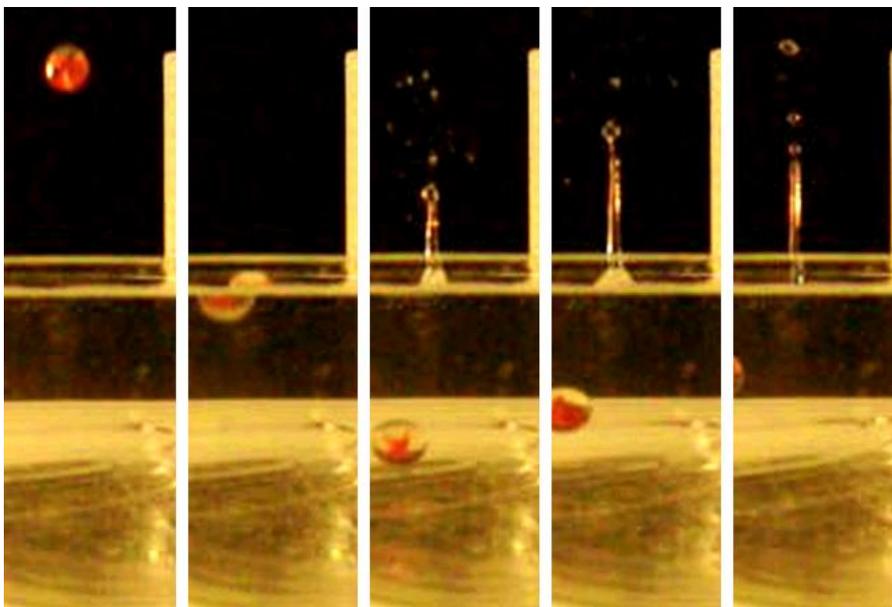


Figure 20. *The course of events that occur during the Worthington jet experiment. A couple of satellite drops are clearly seen in the rightmost picture. The liquid is water.*

Conclusion

The tested polymers do increase the droplet adhesion of aqueous solutions onto hydrophobic surfaces. The amount of polymer in the solution affects the deposition, as well as the type of polymer. An increased molecular weight of the EHEC's increases the deposition effect. The droplet deposition effect for the EHEC and the HEC polymers is correlated to the droplet retraction speed and to the elongational viscosity. A higher retraction speed, as a result of a lower elongational viscosity, results in a larger tendency of the droplet to rebound. However, the result for the cationic polymer deviates from this trend. It enhances the deposition most of all tested polymers, but it still has a high retraction speed, thus it isn't the elongational viscosity that is behind the deposition effect for the cationic polymer, but something else. Addition of polymers to an aqueous solution containing a currently used adjuvant, a surfactant, has shown to increase the droplet adhesion at concentrations below CMC. However no significant difference is seen at concentrations higher than CMC, since the low surface tension, along with a reservoir of surfactants in micelles, makes the droplets prone to flow off the surface. An alternative, to adding polymers to the currently used surfactant solution, is to lower the amount of surfactant to achieve larger droplets and add polymers for the deposition enhancing effect. This leads to less drift while having as good deposition as before. The optimal polymer concentration for the application is between 0.04 % and 0.1 %, since the additional effect of higher concentration is low. The shear viscosity of the polymer solutions at this concentration is very low, which means that the shear viscosity most certainly shouldn't be a problem when spraying these solutions.

Future work

It would be interesting to study the interactions between the polymers and the surfactant more thoroughly. The effect of added pesticide to the solution is important to study, to see whether the deposition effect last or if it changes. The effect of changes in DS_{EO} , MS_{ethyl} , amount of hydrophobic side groups etc. in cellulose based polymers would be interesting to study in order to understand what characteristics is the most important for the deposition enhancing effect. It would also be interesting to evaluate droplet size distribution upon atomization and droplet impact onto hydrophobic surfaces when using similar spraying equipment as the farmer uses. To try a pesticide solution, containing both polymer and surfactant, in real field trials to be able to evaluate the actual effect it has on the bio efficacy would also be very interesting. It would be very useful to understand the mechanism behind why the cationic polymer increases the deposition.

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References

- Bergeron V (2003) Designing intelligent fluids for controlling spray applications. C.R. Physique 4 pp. 211-219.
- Bergeron V, Bonn D, Martin J Y, Vovelle L (2000) Controlling droplet deposition with polymer additives. Nature 405 pp. 772-775.
- Bergström L, Kirchmann H, Thorvaldsson G (2008) Widespread opinions about organic agriculture – are they supported by science evidence? Organic Crop Production – Ambitions and Limitations. Springer, Dordrecht. pp. 1-13.
- Buchholz A (2006) Characterization of the diffusion of non-electrolytes across plant cuticles: properties of the lipophilic pathway. Journal of Experimental Botany. 57 (11) pp. 2501-2513
- Cheny J M, Walters K (1996) Extravagant viscoelastic effects in the worthington jet experiment. J. Non-Newtonian Fluid Mech. 67 pp. 125-135.
- Cheny J M, Walters K (1999) Rheological influences on the splashing experiment. J. Non-Newtonian Fluid Mech. 86 (1-2) pp. 185-210.
- Dexter R W (1996) Measurement of extensional viscosity of polymer solutions and its effects on atomization from a spray nozzle. Atomization and sprays 6 pp. 167-191.
- Ergungor Z, Smolinski J M, Manke C W, Gulari E (2006) Effect of polymer-surfactant interactions on elongational viscosity and atomization of peo solutions. J. Non-Newtonian Fluid Mech. 138 pp. 1-6.
- FAO (Food and agriculture organization of the united nations) (2006) <http://faostat.fao.org/site/339/default.aspx>, cited 10 may 2010.
- Holmberg K, Jönsson B, Kronberg B, Lindman B (2007) Surfactants and polymers in aqueous solutions 2nd edition. Wiley, Chichester.
- Karlsson L (2002) Hydrophobically modified polymers - rheology and molecular associations. PhD thesis, Lund University, Lund.
- Kennedy J C, Meadows J, Williams P A (1995) Shear and extensional viscosity characteristics of a series of hydrophobically associating polyelectrolytes. J. Chem. Soc. Faraday Trans. 91(5) pp. 911-916.
- Mezger T G (2006) The rheology handbook 2nd edition. Vincentz Network, Hannover
- Mun R P, Young B W, Boger D V (1999) Atomization of dilute polymer solutions in agricultural spray nozzles. J. Non-Newtonian Fluid Mech. 83 pp. 163-178.

Ng S L, Mun R P, Boger D V, James D F (1996) Extensional viscosity measurements of dilute solutions of various polymers. *J. Non-Newtonian Fluid Mech.* 65 pp. 291-298.

Phillips Mcdougal 2007 Agriservice database.

Rodd L E, Scott T P, Cooper-White J J, McKinley G H (2005) Capillary break-up rheometry of low-viscosity elastic fluids. *Appl. Rheol.* 15 pp. 12-27

Schönherr J (2006) Characterization of aqueous pores in plant cuticles and permeation of ionic solutes. *Journal of Experimental Botany* 57 (11) pp. 2471-2491

Smith D E, Chu S (1998) Response of flexible polymers to a sudden elongational flow. *Science* 281 pp. 1335-1340.

WA Forster et al. (2001) in *Proceedings 6th International Symposium on Adjuvants for Agrochemicals*, Ed.: H De Ruiter. Amsterdam, The Netherlands, pp. 35-40.

Westbye Peter (2008) *Self-assembly of hardwood xylan – in aqueous solution and at cellulosic surfaces*. PhD thesis, Chalmers University of Technology, Göteborg.

Wirth W, Storp S, Jacobsen W (1991) Mechanisms controlling leaf retention of agricultural spray solutions. *Pestic. Sci.* 33 pp. 411-420.

Zabkiewicz J A (2007) *Spray formulation efficacy – holistic and futuristic perspectives*. *Crop Protection* 26 pp. 312-319.