

INVESTIGATION OF THE FOULING BEHAVIOUR OF A POLYMER DURING SYNTHESIS

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ABSTRACT

During the synthesis and processing of polymers, a significant amount of polymer may be deposited on the heat transfer surfaces. This study deals with the fouling behaviour of a vinyl acetate vinyl ester copolymer during emulsion polymerisation. The influence of the state of polymerization and the wall temperature was investigated. Experiments were performed in a 5 L reactor system combined with a flow channel. By using a fluidic heated or cooled flow channel it is possible to carry out investigations on heated or cooled surfaces. The deposition was quantified by the mass-based fouling resistance, by a gravimetric calculation of the fouling mass, the height of the fouling layer and the surface coverage using a digital microscope. It was shown that the state of polymerization and the temperature have a strong influence on the fouling behaviour, especially on the structure of the fouling layer.

INTRODUCTION

Emulsion polymerization is currently the preferred process for the commercial production of vinyl acetate, chloroprene, various acrylate copolymerization and copolymerization of butadiene with styrene and acrylonitrile (O'dian, 2004). The polymerization process is frequently accompanied by the formation of deposits on the internal surfaces of the polymerization reactors (reactor wall, baffles, impeller). This deposition which occurs during the synthesis of polymers is referred to as polymerization fouling. The fouling layer on the heat-transferring surface forms an additional heat conducting resistance and reduces the efficiency of the heat exchanger. This increases the required heat transfer area for a given production capacity as well as the energy demand and thus ultimately increases CO₂ emission.

This study deals with polymerization fouling which forms during emulsion polymerization. A review of chemical reaction fouling, primarily of organic fluids, was given by Watkinson and Wilson (1997). Fouling during emulsification polymerization was recorded by Vanderhoff (1981).

Here fouling is defined as coagulation of latex particles in consequence of instabilities. Because different substances and reactions may be involved during synthesis, there is no general knowledge of polymerization fouling (Bott, 1995). The deposition processes in general are still mostly unknown and there are only very substance-specific publications. Looking at the literature in the field of organic fouling, a major focus on auto-oxidation is found. Polymerization, on the other hand, has been given little consideration (Watkinson and Wilson, 1997). Buchelli et al. (2005) have investigated the fouling behavior of low-density polyethylene (LDPE) in a tubular reactor. The focus was on the determination of the fouling layer thickness in an industrial polymerization reactor based on plant data and heat transferring models. Tabrizi and Fadae (2017) addressed the applicability of two conductivity sensors for the investigation of fouling deposits during emulsion polymerization of different model material systems. Both studies deal with detection possibilities and less with the deposition mechanism itself. Cunningham and O'Driscoll (1991) investigated the conditions under which fouling occurs in tubular polymerization reactors using bulk methyl methacrylate polymerizations. They demonstrated that reactor orientation and flow direction have a significant effect on fouling behavior. Gottschalk et al. (2015) carried out initial investigations of a vinyl acetate-based copolymer. It was shown that fouling can be reduced by modifying the surface with diamond-like carbon coatings. All of these publications only deal with very specific influencing factors and resulting phenomena, but little work has been reported on the basics of the deposition mechanism.

The purpose of this study is to obtain general information on polymerization fouling during emulsion polymerization of a vinyl acetate vinyl ester copolymer. For this purpose, four situations are defined in which polymer deposits can occur: during synthesis (polymerization fouling), during further processing of the already reacted polymer (polymer fouling), as well as on heated and cooled surfaces (Fig. 1). In particular, the comparison to polymer

fouling is used to develop a broader understanding and to work out the special features of polymerization fouling.

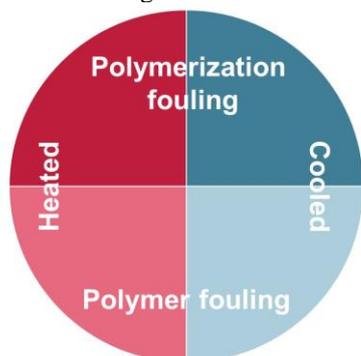


Fig. 1. Schematic classification of the addressed fouling situations

The four quadrants are examined separately in order to be able to draw conclusions about the deposition behavior during emulsion polymerization based on possible differences and similarities. The focus will be on polymerization fouling on heated surfaces.

EXPERIMENTS

Model fouling system

Polymerization fouling experiments are performed during a radical emulsion polymerization of a vinyl acetate / vinyl ester copolymer (see Fig. 2) as model synthesis. Vinyl acetate and vinyl ester are used as monomers. Ascorbic acid and tert-butyl hydroxiperoxide (TBHP) act as initiators. The system is stabilized by an aqueous polyvinyl alcohol solution (PVOH). Polymer fouling experiments are performed with a vinyl acetate, ethylene copolymer dispersion (VINNAPAS®LL6120, see Fig. 2) provided by Wacker Chemie AG, Germany. In this case polymerisation has been terminated, i.e. the broth is dead

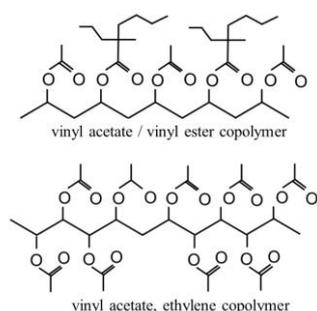


Fig. 2. Structural formula of the material systems

Both systems are colloidal stabilized latex particles in PVOH as continuous phase and have a droplet size of approx. 1 μm .

Fouling experiments

The fouling investigations are performed in a reactor system combined with a flow channel. The

reaction vessel serves as a storage vessel in which the reactants are mixed and preheated while the flow channel represents the heat-transferring surface for the fouling investigations. The reactor system consists of a 5 L double-walled reaction vessel in which the monomers are dosed with the use of a peristaltic pump. The reaction process is controlled by the reactor temperature, which is recorded online by means of a thermocouple. The flow channel is operated in a loop and can be cooled or heated by a fluid in countercurrent flow, as shown in Fig. 3. Inside the flow channel a stainless-steel plate with $w \times l \times h = 20 \times 80 \times 2 \text{ mm}$ is fixed on which the fouling tests are carried out. The initiator is added upstream to the inlet of the flow channel, so that the reaction takes place inside the flow channel. The initiator reacts with the monomers within 3 seconds and the mean residence time of the fluid in the flow channel is greater than 3 seconds. Therefore, a large part of the initiator should already react in the flow channel. Should free radicals still be present when entering the reservoir, they would still react there, but this is irrelevant for the experiment.

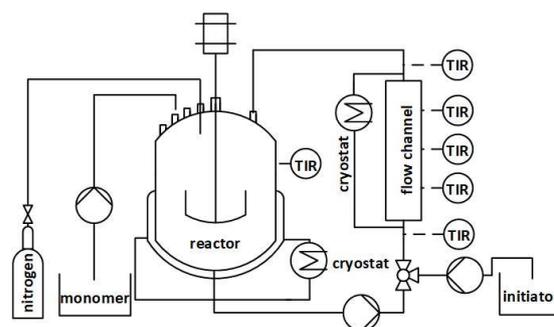


Fig. 3. Flow chart of the experimental set-up

With this experimental set-up, it is possible to carry out fouling investigations of a reacting material system on heated as well as on cooled surfaces. The reactor can also be used as a storage vessel for an already reacted polymer dispersion, so that reacting systems can be compared with already reacted systems in the same setup, i.e. under the same test conditions. At the beginning of an experimental run, part of the monomers, the polyvinyl alcohol solution and the ascorbic acid are filled into the reactor and mixed at 200 rpm. After preheating the reaction mixture to 55 $^{\circ}\text{C}$, the reaction is started by adding the TBHP. The start of the reaction is indicated by a significant increase in temperature. The reaction takes place at a temperature of 67 $^{\circ}\text{C}$. After the reaction has started, a defined conversion profile is followed by adding further monomer mixture and initiator. The conversion is determined on the basis of the solids content. The solids content c_{Polymer} can be determined via the density ρ_{Polymer} , as they are proportional to each other. The density, which can be measured, depends on the chain length and this determines the solids content. The solids content can

be calculated from the density via an almost linear correlation.

To check whether the desired conversion has been achieved, the solid content is determined after 30, 50, 120 and 210 minutes and after the reaction has been stopped. After the monomer has been completely added, the initiator dosage is increased in order to post-polymerize the remaining free reactants. This can be recognized by a renewed rise in temperature. A subsequent temperature decrease indicates that all the monomer has reacted and the reaction is terminated.

Optical measurement

A record of the fouling layer as well as the surface roughness was measured optically with a Keyence digital microscope VHX 6000. A 2D image of the entire plate was taken at 50 x magnification as well as three partial images (20 x 5 mm) at the inlet (Pos. 1), the middle (Pos. 2) and the outlet (Pos. 3) of the substrate are taken at 200x magnification (see Fig. 4). To characterize the surface roughness the arithmetical mean height S_a and the maximum height S_z were determined at all three positions optically by light scattering via ISO 25178. S_a is the extension of the arithmetical mean height of a line R_a to a surface. As an absolute value it expresses the difference in height of each point compared to the arithmetical mean of the surface. This parameter is used generally to evaluate surface roughness. S_z is defined as the sum of the largest peak height value and the largest pit depth value within the defined area. Due to the transparency of the sample a minimum detectable change in surface roughness of $\pm 1 \mu\text{m}$ is possible.

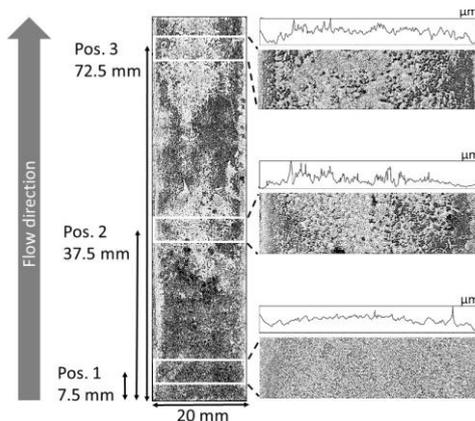


Fig. 4. Microscopic images of the substrate including the measuring points

The height of the fouling layer x_f is also obtained for the three partial images. It is determined from the ratio of volume to surface area of the observed section and therefore describes an average layer height.

Fouling resistance

The thermal fouling resistance is calculated as the difference between the thermal resistance $1/k(t)$ of the contaminated surface at time t and the resistance of the clean surface at the beginning of the test $1/k_0$.

$$R_f(t) = \frac{1}{k(t)} - \frac{1}{k_0} \quad (1)$$

Due to the liquid temperature control and the changing material properties (temperature, viscosity, density) during the reaction, a constant heat flow cannot be assumed, whereby a direct calculation of the thermal fouling resistance from the temperature curves is not possible. Therefore the mass based fouling resistance $R_{f,m}$ and a fouling resistance calculated from the layer height $R_{f,x}$ are used instead of the thermal fouling resistance.

$$R_{f,m} = \frac{m_f}{\rho_f \cdot \lambda_f} \quad (2)$$

$$R_{f,x} = \frac{x_f}{\lambda_f} \quad (3)$$

$R_{f,m}$ was calculated from the fouling mass m_f and $R_{f,x}$ was calculated from fouling layer thickness x_f , under the assumption that a uniform fouling layer with a constant density ρ_f and thermally conductive λ_f is formed of the fouling layer.

RESULTS AND DISCUSSION

Establishment of a stable polymerization reaction

In order to be able to carry out fouling investigations during synthesis, first it is necessary to operate a stable and reproducible polymerization reaction. The temperature and solids content are particularly important as these two parameters have a significant influence on the fouling behavior. Fig. 5 shows a typical bulk temperature curve in the reactor, the temperature of the bulk at the inlet and outlet of the flow channel as well as the average wall temperature.

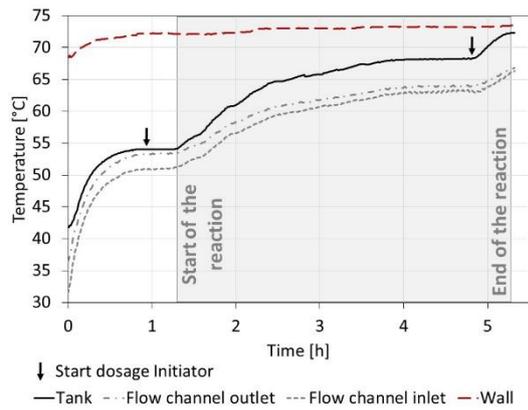


Fig. 5. Temperature curve of the reaction

The reaction start can be recognized by an increase in the reactor temperature as well as an increase in temperature in the flow channel. The reaction normally starts at an average of (33.5 ± 3.5) min after the initiator dosing has started. The starting time of the initiator addition is marked with a black arrow. During the experiment, the reactor temperature rises from 55 °C to approx. 67 °C; the temperature in the flow channel is slightly below the reactor temperature at 64 °C. During the synthesis, the wall temperature stays almost constant 73 °C, so that the driving temperature difference decreases during the experiment. The post-polymerization can be recognized by a renewed temperature rise to a final reactor temperature of 72 °C and 67 °C in the flow channel. Fig. 6 shows the conversion quantified by the solid content over the experimental time. The conversion is measured in the reactor, but this is equivalent to the conversion in the flow channel.

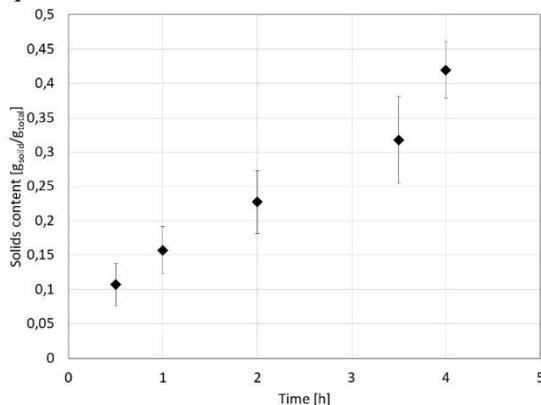


Fig. 6. Conversion curve during reaction

This is the decisive parameter to show the reaction success and the reproducibility of the synthesis. In addition, the solids content has a strong influence on the fouling behavior. Half an hour after the start of the reaction, the solids content is 0.10 $\text{g}_{\text{solids}}/\text{g}_{\text{total}}$ and increases to 0.42 $\text{g}_{\text{solids}}/\text{g}_{\text{total}}$ during the reaction. The density and viscosity of the polymer also change proportionally to the solids content and with the changing material properties

the flow properties quantified by the Reynolds number change as well, see Table 1.

Table 1. Change of density, viscosity and Reynolds number from start to end of the reaction

	0.10 g solid/g total	0.42 g solid/g total
ρ [g/cm^3]	0.98773	1.043
η [mPas]	2.35	172
Re [-]	513	7

As a result of the increasing solids content over the reaction time, the Reynolds number decreased from 513 to 7. The final solids content varies with (0.42 ± 0.04) g solids/g total. This deviation causes a change in the Reynolds number of 5 - 10, which is negligible.

Polymerization vs. polymer fouling

In order to obtain first information about the difference between polymerization and polymer fouling, an optical observation was carried out. For this purpose, the whole sample plate was examined under the digital microscope. The image was taken by combining several single images automatically at 50x magnification. The results are shown in Fig. 7.

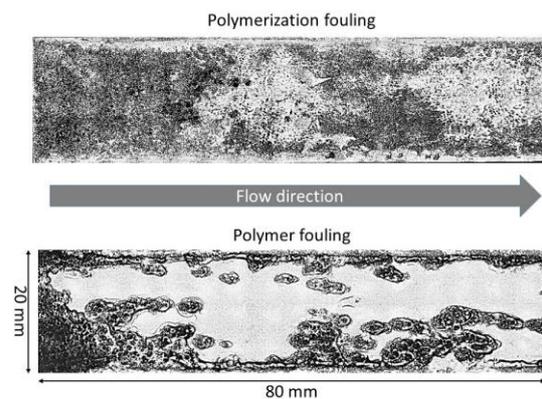


Fig. 7. Microscopic image of fouling layer on a heated surface, polymerization fouling (top) and polymer fouling (bottom)

In addition, for three sections of 20 x 5 mm at the inlet (Pos. 1), the middle (Pos. 2) and the outlet (Pos. 3) of the substrate, roughness profiles were examined at 200x magnification. Both experiments were carried out on a heated surface with a wall temperature T_w of 73 °C, a bulk temperature T_b of 65 °C and a volume flow of 50 l/h. During the polymerization reaction, the solids content increases to 0.38 g solids/g total. Correspondingly an equivalent solids content to the end of the reaction of 0.38 g solids/g total was selected for the polymer fouling experiments.

Comparing the fouling layer of both experiments, a clear optical difference can be seen. The upper

picture shows the fouling layer of the polymerization fouling experiment, the lower one shows the fouling layer of the polymer fouling experiment. During polymerization fouling, a nearly compact polymer film with many small elevations is formed. Less strongly covered areas appear white and are difficult to recognize due to the semi-transparent polymer. Fig. 8 presents an image of the fouling layer under the scanning electron microscope. It shows a compact but very uneven polymer film with many drop-shaped elevations. The size of the droplets varies from a few micrometres to approx. 50 μm . The roughness profile will be discussed in more detail below. An almost identical particulate morphology was also observed by Wilson and Watkinson (1996) in a fouling layer of lube oil on a heated surface, with gum globule dimensions of approximately 7-20 μm . The deposition process there was explained by autoxidation. In comparison during polymer fouling, optically visible polymer is deposited only in parts of the surface. Most of the deposit is located at the edge and at the inlet of the substrate. The strong deposition at the edge of the substrate can be explained by the parabolic velocity profile of the laminar flow in the flow channel. The flow velocity is lowest in the edge areas, which also reduces the shear stress, so that less material will be removed.

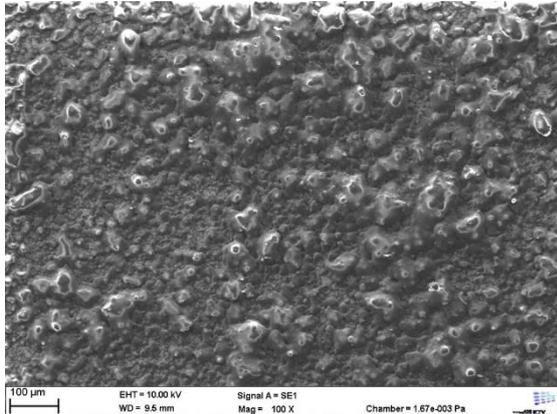


Fig. 8. SEM picture of the fouling layer from polymerization fouling

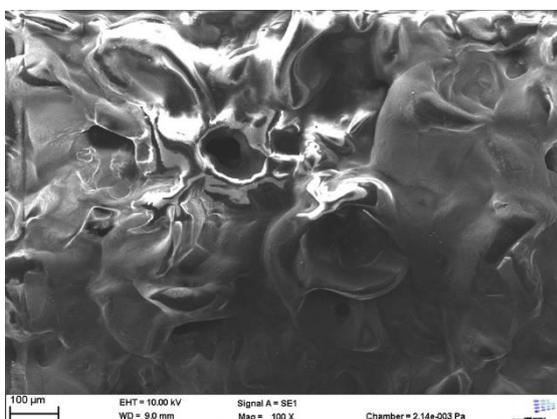


Fig. 9. SEM picture of the fouling layer from polymer fouling

The areas covered have a crater like structure which can be seen in Fig. 9. The craters have a diameter of up to 100 μm and are visible even without magnification. Such a structure was also found by Gottschalk et al. (2015) during polymer fouling experiments on different heated surfaces. Since the boiling temperature of the polymer dispersion with 100 $^{\circ}\text{C}$ is far above the wall temperature with 73 $^{\circ}\text{C}$, this structure cannot be the result of an evaporation process, because the polymer is still not boiling. The exact mechanism for the formation of this crater structure is not yet known. The structure is possibly due to a local destabilization of the dispersion due to phase inversion.

For the characterization of surface roughness, the maximum height S_z and the arithmetical mean height S_a , for polymerization fouling (left) and polymer fouling (right) are shown in Fig. 10. Comparing the surface roughness of the fouling layers of both tests, the arithmetic mean height S_a of the polymer fouling test with 120 μm is much higher than that of the polymerization fouling test of only 23 μm . Especially during polymer fouling, S_a fluctuates strongly over the entire plate.

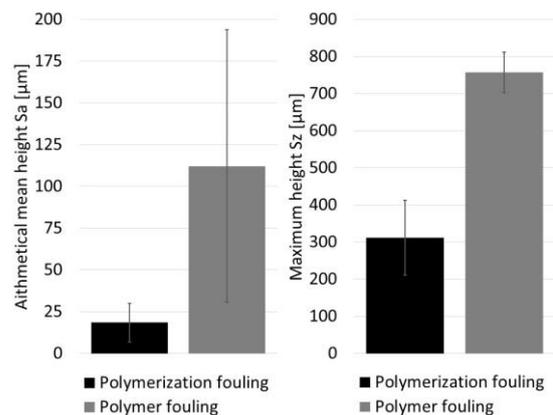


Fig. 10. Arithmetical mean height S_a (left) and maximum height S_z (right) of the fouling layers from polymerization fouling and polymer fouling on a heated surface

This is due to the uneven deposition patterns over the plate and the crater structure described above. The maximum height S_z is also larger for the polymer fouling layer. S_z reaches values of 310 μm for polymerization fouling and 760 μm for polymer fouling. These high values are also caused by the strongly shaped crater structure with the many elevations. Overall, despite identical process conditions (flow velocity, temperature gradients, chemical composition), there is a clear optical difference between the two fouling situations, the only difference being the state of polymerization of the material system (reacting vs. already reacted), which suggests that this has a decisive influence on the deposition behavior. These initial studies show that there is a different deposition behavior during

polymerization fouling and polymer fouling, the cause of which needs further investigation before conclusions can be drawn about the deposition mechanism.

Heating vs. cooling

Apart from the state of polymerization, the influence of the wall temperature was investigated. In addition to the heated surface $T_w > T_b$, investigations without heat dissipation or supply $T_w \approx T_b$ as well as investigations on cooled surfaces $T_w < T_b$ were conducted during polymerization fouling. During polymer fouling, investigations were carried out only on heated surfaces and without heat dissipation or supply. The deposition on a cooled surface is not considered here, because the deposition was so little that it was hardly measurable. Due to the reaction, no direct influence can be exerted on the bulk temperature or the solid concentration, which is why these are largely constant. However, there is a slight change in temperature along the flow channel, the influence should also be taken into account. Table 2 shows the varied parameters. All experiments were carried out with a solid content of $0.38 \text{ g}_{\text{solids}}/\text{g}_{\text{total}}$ and a volume flow rate of 50 l/h. The bulk temperature varies by 7 K due to the constant heat of reaction and the varied wall temperature. The variability of the bulk temperature seems to have no influence on the conversion of the reaction, as all tests show a similar solids content at the end of the test ($C_{\text{Polymer}} = 0.42 \pm 0.04 \text{ g solids/g total}$).

Table 2. Wall and bulk temperature of the test series run

	Polymerization fouling	Polymer fouling
$T_w < T_b$	$T_w = 15.5 \text{ }^\circ\text{C}$ $T_b = 58.2 \text{ }^\circ\text{C}$	-
$T_w \approx T_b$	$T_w = 60 \text{ }^\circ\text{C}$ $T_b = 60.3 \text{ }^\circ\text{C}$	$T_w = 60 \text{ }^\circ\text{C}$ $T_b = 60.5 \text{ }^\circ\text{C}$
$T_w > T_b$	$T_w = 73.5 \text{ }^\circ\text{C}$ $T_b = 65.5 \text{ }^\circ\text{C}$	$T_w = 73 \text{ }^\circ\text{C}$ $T_b = 64.5 \text{ }^\circ\text{C}$

Influence of the wall temperature

The influence of wall temperature was investigated with the use of the fouling layer height and the fouling mass. Using the digital microscope,

the mean layer height of the different fouling layers was determined. These are shown in Fig. 11.

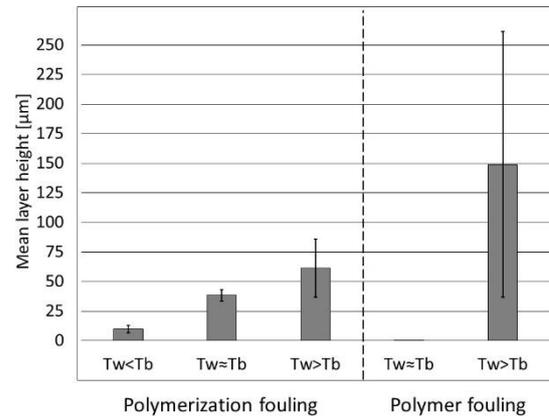


Fig. 11. Mean layer height of the tests heated, without heat dissipation and cooled during polymerization fouling and polymer fouling

As the wall temperature rises, an increase in the layer height can be seen both during the polymerization fouling and during the polymer fouling process. According to literature, the deposition of organic substances increases with increasing heating area following an Arrhenius approach (Müller-Steinhagen, 1993). During polymer fouling, on the surface without heat dissipation $T_w \approx T_b$, the deposit of less than one micrometer is almost undetectable. By contrast, considerably more is deposited on the heated surface. The high standard deviation is particularly noticeable here. An average layer height of $150 \text{ } \mu\text{m}$ is achieved on the heated surface. The values fluctuate strongly, since the layer height was averaged over the entire sample plate and especially at the channel inlet it is comparatively high with more than $300 \text{ } \mu\text{m}$. The course of the layer height along the plate is discussed in more detail below. If one compares the deposition of polymerization fouling experiments with those of polymer fouling, particularly on the heated surface, strong differences can be seen. More than twice as much polymer is deposited during polymer fouling.

In addition to the layer height, also the fouling mass was determined. In order to compare the results of these measurements with the layer height, both parameters were converted into fouling resistances, see Table 3.

Table 3. Comparison of the mass-related fouling resistance with the layer height related fouling resistance

	m_f [mg]	R_{fm} [$10^{-4} \frac{m^2}{W K}$]	R_{fx} [$10^{-4} \frac{m^2}{W K}$]
Polymerization fouling			
$T_w < T_b$	1.5	0.04	0.4
$T_w \approx T_b$	18.0	0.51	1.73
$T_w > T_b$	106.4	3.00	2.76
Polymer fouling			
$T_w \approx T_b$	11.0	0.30	0.02
$T_w > T_b$	216.7	7.35	6.70

The deposited fouling mass as well as the layer height increase with increasing wall temperature. Comparing the mass-related fouling resistance with the layer height, both show a similar trend. For the larger fouling resistances the two calculated fouling resistances match well, but for the smaller ones they strongly deviate. There seems to be no systematic error here. The deviation is due to the measurement uncertainty of the digital microscope as well as the gravimetric determination. Thinner films are more transparent and harder to capture with a digital microscope. Overall, it is possible to compare the fouling deposition both via the mass and via the layer height. However, absolute values should be considered with caution, especially for small depositions. The disadvantage of the mass-related fouling resistance is that only an integral consideration is possible. An incremental fouling resistance can be determined via the layer height by measuring the substrate segment by segment.

Influence of the bulk temperature

Furthermore, the distribution of the layer height along the substrate was investigated. For these investigations the state of polymerization was neglected at first and only polymerization fouling experiments was considered.

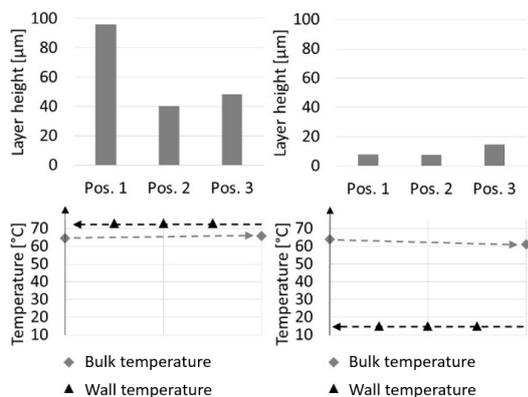


Fig. 12 presents the layer height along the plate on a heated surface (left) and on a cooled surface (right). The layer height decreases by about 50 % on the heated surface from the inlet to the outlet and an increase by about 50 % on the cooled surface.

Overall, however, as described above, more polymer is deposited on the heated surface than on the cooled surface, which can be explained by the higher wall temperature. The layer height along the substrate cannot be explained by the wall temperature, since it is almost constant. However, the bulk temperature changes minimally along the substrate. The bulk temperature increases from 64.5 °C on the heated surface by 1.5 K, and decreases from 64 °C on the cooled surface by 3 K.

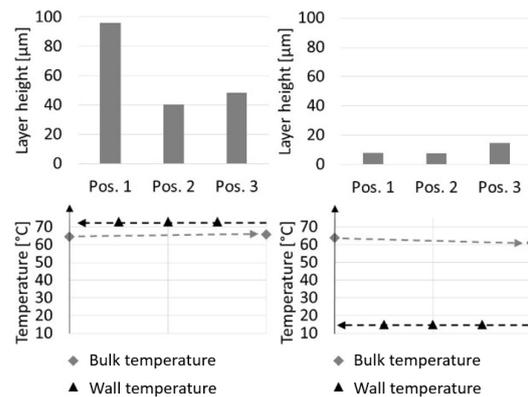


Fig. 12. Investigation of the layer height distribution along the substrate, considering the wall and bulk temperature

Nonetheless, the larger temperature difference between the inlet and outlet on the cooled surface does not result in a larger layer height difference compared to the heated surface. The bulk temperature thus seems to have a minor influence on the layer height, but the influence of the wall temperature predominates significantly. The material properties of the suspension also change due to the changing bulk temperature. This change is too small to explain the layer-height-progression. Due to the temperature drop of 3 K, the viscosity changes only from 106 mPa·s to 122 mPa·s at a solid's content of 0.38 g polymer/g total. This causes a negligible change in the Reynolds number. Further influencing factors, such as the alignment of the channel or a change in the concentration along the channel, cannot be excluded so far.

CONCLUSION

In this study, the fouling behavior of a vinyl acetate vinyl ester copolymer during emulsification polymerization was investigated and compared to the fouling behavior of an already reacted polymer. Furthermore, the influence of the wall temperature was addressed. At first, a plant concept was presented which allows the investigation of both reacting and already reacted material systems on cooled and heated surfaces. It was shown that it is possible to carry out a reproducible reaction and to determine the influence of the changing material

properties on the fouling. The focus of the investigations was on the influence of the state of polymerization. It was found that a reacting material system shows a different deposition behavior in form and structure than an already reacted material system. Furthermore, an increase of the wall temperature leads to an increased polymer deposition during polymerization fouling as well as during polymer fouling. In addition, a change in the layer height along the channel was observed which is mainly attributed to the changing bulk temperature. In the following investigations, the influence of the temperature will be addressed in more detail. In addition, the influence of the alignment of the channel has to be excluded. In order to gain more detailed knowledge about polymerization fouling during emulsion polymerization, a focus will be placed on the analysis of the deposited material.

NOMENCLATURE

c	solid content, g solid/g total
h	height, mm
k	heat transfer coefficient, W/(m K)
l	length, mm
m_f	mass, mg/cm ²
R_a	height of a line, μm
Re	Reynolds number, dimensionless
R_f	Fouling resistance, m ² K/W
S_a	arithmetical mean height, μm
S_z	maximum height, μm
T	temperature, °C
w	width, mm
x_f	layer height, μm
ρ_f	density of the fouling layer, g/cm ³

Greek symbols

η	dynamic viscosity, kg/(m s)
ρ	density, g/cm ³
λ	thermally conductive, W/m ² K

Subscript

0	initial
b	bulk
f	fouling
m	mass
w	wall
x	layer height

Acronyms

LDPE	Low density polyethylene
PVOH	Polyvinyl alcohol
rpm	Revolutions per minute
SEM	Scanning electron microscope

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