CHEMICAL ENGINEERING TRANSACTIONS

VOL. 29, 2012

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Hon Loong Lam, Jiří Jaromír Klemeš

ISBN 978-88-95608-20-4; **ISSN** 1974-9791 DOI: 10.3303/CET1229226

Challenges in Design of Polymer Falling Film Heat Exchangers

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Due to economic considerations polymer construction materials become an important alternative in apparatus design. Also a requirement of metal-free products (pharmaceutical or food industries) or the handling of corrosive fluids demands innovative heat exchanger materials. Therefore the existing concept of a polymer film heat exchanger should be optimized to make it a more competitive alternative to common devices. Different polymers are characterized due to their surface free energy and falling film wettability as well as their mechanical limits. The wetting behaviour of the surfaces is successfully improved by physical surface treatments and is stated for different temperatures. The limiting mechanical values stayed unaffected to the treatments.

1. Introduction

Since the prizes for metal or metallic alloys increases polymer construction materials are a reasonable alternative in heat exchanger design. The resistance to corrosion and the adhesion properties related to scaling deposits are further advantages of polymer surfaces. An overview of the use of polymers in heat exchangers are given by Reay (1989) and the review of Zaheed and Jachuck (2004). Most of the manufactured polymer heat exchangers are designed as spirals or bundled tubes. To compensate the low thermal conductivity the heat transfer surface can be realized as a thin film. Scheffler and Leao (2008) reported about the fabrication of polyolefin heat transfer surfaces. Christmann et al. (2010) applied a polyetheretherketone (PEEK) film as heat transfer surface and reached mean overall heat transfer coefficients up to 1570 ± 181 $W \cdot m^2 \cdot K^{-1}$ dependent on the operating conditions. These values were achieved by a modification due to the wetting degree of the heat transfer surface. For more efficient polymer heat exchanger processes the wettability has to be improved significantly. The required research should focus on a detailed understanding of the interactions at the solid-liquid interface. Besides surface treatments to change the functionality of the polymer surface also structural and geometrical optimization can lead to a wetting improvement due to hydrodynamic effects.

The challenge in surface optimization and apparatus design consists in the complex dependency of all parameters of interest. A change of the wetting behavior by a surface treatment also changes the sensitivity to fouling and the mechanical stability due to emerging interactions with the process media. Hence in this paper physical surface treatments are studied with respect to their influence on the wetting behavior. To differ between wetting improvements due to molecular surface changes and macroscopic hydrodynamic effects, experimental work at different scales is presented. Contact angle measurements should be compared to falling film wetting experiments both including temperature variations. The impact of the treatments on the mechanical parameters is considered in tensile tests.

Please cite this article as: Dreiser C. and Bart H.-J., (2012), Challenges in design of polymer falling film heat exchangers, Chemical Engineering Transactions, 29, 1351-1356

2. Experimental

2.1 Methods

The small scale wetting properties of a surface are mainly driven by the equilibrium at the interface of solid, liquid and surrounding gas-phase. The contact angle between the wetting liquid and the solid surface at the triple point is essential to characterize a surface. Young (1805) correlated the contact angle to the surface free energy and the interfacial tensions. Therefore contact angle measurements were carried out with an OCA 15 EC setup by Dataphysics. The SCA20 software allows an accurate control of the droplet volume and supports the analysis of the CCD camera images. External influences can be neglected by the use of a temperature-controlled syringe and sample support plus an air conditioner. Electrostatic charges of the polymers are avoided by the grounding of the sample support. Each contact angle measurement was executed with a sample number of ten droplets with a droplet volume of 3 to 10 µL dependent on the used liquid. The droplet shape was fitted with an ellipse which generates two contact angles for one droplet. Changes in the surface free energy were calculated with the method developed by Wu (1971) where the polar and disperse parts of the surface free energy are calculated by a harmonic mean. This method is recommended for low energy materials like unmodified polymers. By the measurement of pendant drops against a reference fluid the liquid surface tension components can be derived. To describe the Lewis acid and base components of the polar part the model of van Oss et al. (1988) and van Oss and Good (1989) was used. In this case the disperse part is described as a Lifshitz - van der Waals component. Here the components for the used liquids were taken from literature (Birdi, 1997; van Oss et al. 1989).

Besides the influence of molecular changes of the surface texture the macroscopic changes of the surface topology does also influence the wetting characteristics. Wenzel (1936) for example described the dependence for a single droplet wetting by the introduction of the roughness factor *r* as a direct proportion between the quotient of the rough and ideal smooth surface area and the quotient of the cosine of the according measured static contact angles. To differ between the wetting shift due to surface energy changes and topology as well as geometric effects larger scale wetting experiments are necessary to describe the falling film hydrodynamics in comparison to the surface energy determination as a screening method for several fluids. The values of interest are the wetting hysteresis and the minimum wetting rate dependant on the apparatus geometry and the wetted surface.

A lab-scale wetting apparatus represents the geometric similar section of a pilot plant heat exchanger developed by Christmann et al. (2010) to describe the fluid dynamic behaviour of the falling film on the polymers and the influence of the spacer geometry on the hydrodynamics. However, to compare the lab-scale wetting experiments with the polymer surfaces to contact angle measurements and to stainless steel a setup on the flat plane was arranged. The temperature-controlling arrangement allows optional experiments with heat transfer plus the falling film can be temperature-controlled individually as well. The two characteristic minimum wetting rates were determined by a stepwise increase of the liquid load until a closed falling film was established and decreasing until the film break up. The lab-scale wetting hysteresis is described as a relation between relative wetted area and liquid load. Therefore several pictures of the wetted surface were visually analyzed for defined loads to calculate the relative wetted area.

The tensile tests were performed with the materials testing machine Z010 (Zwick GmbH & Co. KG). According to EN ISO 527 five stress-strain diagrams were determined per sample of 20 mm width, 50 mm length and 25 µm thickness with an initial tension of 5 MPa. The Young´s modulus was diagnosed with a strain rate of 1 $mm \cdot min^{-1}$ and calculated with the method of least squares as gradient of the regression line. The remaining data of the curve was collected with a strain rate of 50 $mm \cdot min^{-1}$. To cope with anisotropic properties of some films samples in extrusion direction (ied) and orthogonal to extrusion direction (oed) were prepared and studied. All experimental errors and error bars represent statistical (confident interval of 95 %) and experimental uncertainties.

2.2 Materials

To satisfy the industrial requirements the selected polymers should possess properties like a good mechanical stability due to the pressure drop in heat exchanger operations, a high thermal conductivity, chemical resistance to common solvents as well as to corrosive media and a high operating temperature. Compared to stainless steel 1.4571 as a standard construction material in apparatus design the thermoplastic polymers polypropylene, polysulfone and polyetheretherketone were chosen and allocated as 25 µm films.

All the PEEK films were ordered as an untreated and a plasma treated version. According to Victrex Europa GmbH the treatment was arranged with an atmospheric helium/oxygen-plasma. The ordered PSU films were delivered by Dr. D. Müller GmbH as an untreated and a corona treated option. Together with the untreated PP the studied polymers can be compared to the stainless steel 1.4571 and its electro-polished version. The thermal conductivity and the mechanical properties are attributed to the structure (amorphous: PSU, PP, PEEK APTIV® 2000 and partially crystalline: PEEK APTIV® 1000 and PEEK APTIV® 1103 plus 30 % mineral filler).

3. Results and Discussion

Plasma and corona treatments represent common options of surface engineering to change the surface free energy of polymers. Figure 1 shows how the different parts of the overall energy change.

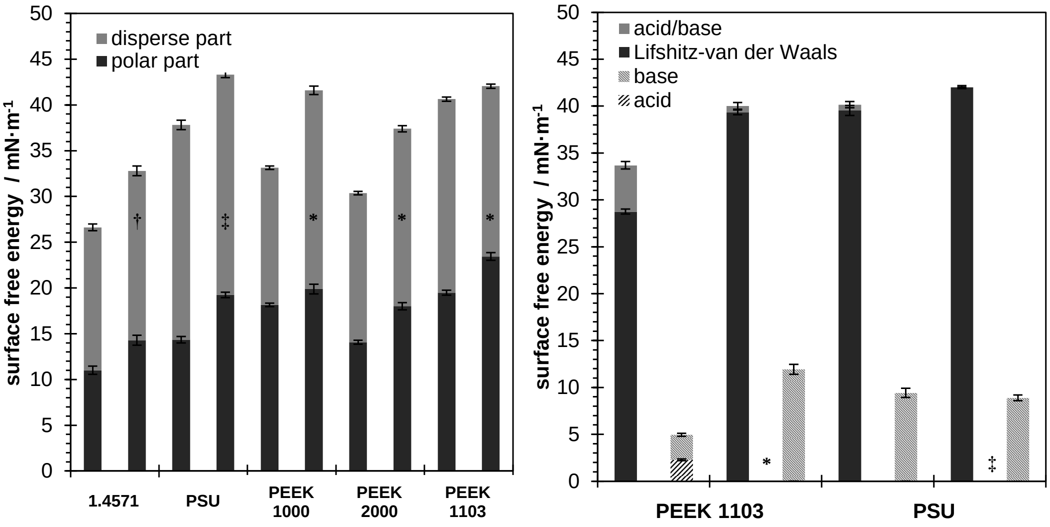

*Figure 1: Surface free energy and its polar and disperse component (left) and its Lifshitz-van der Waals and acid/base component (right) for stainless steel 1.4571, polysulfone and polyetheretherketone variations dependent on different surface treatments (†: electro-polished, ‡: corona treatment, *: plasma treatment)*

Due to all physical surface treatments the overall surface free energy of the materials is improved. In nearly all cases the polarity, the ratio of polar part and overall surface free energy, improves as well. The van Oss-model is very sensitive to small deviations in all input values (measured contact angles and surface energies of the used liquids). However, this method allows a qualitative impression on the induced changes in molecular scale. For instance the mineral filled partially crystalline film PEEK APTIV® 1103 experiences an increase of the Lifshitz-van der Waals component and also a shift from a bipolar to an approximately monopolar-basic surface. The unspecific oxidation of the plasma treatment increases the carbonyl and ether groups. The polysulfone film changes from an approximately monopolar-basic to a definite monopolar-basic surface after the corona treatment (acid part changes from 0.01 to 0.00 mN·m^{-1}). Here the ether and sulfonyl groups are responsible for a high basic part.

Both polymers share benzyl groups where the delocalized π-electrons contribute also to the basic character. Only a detailed study with spectroscopic methods can clarify the real composition of the functional groups on the polymer surface after the treatment. After a successful surface optimization with respect to the wetting behavior further boundary conditions need to be considered for the heat exchanging process.

Mechanical investigations of the different polymer films and a sound knowledge of possible anisotropic effects are essential for a solid apparatus design. Exemplarily stress-strain diagrams resulting from tensile tests are shown in Figure 2. Obviously the crystallinity and type of polymer has a big influence on the yielding of the polymers. However, the operational stress area as a result of pressure difference must always be correlated below the yield point of the selected material. In this linear area of stress-strain relationship the Young´s modulus can quantify the material characteristics. Relating to Figure 2 the Young´s modulus is unaffected to the physical surface treatments, which was also obtained for the tensile strength.

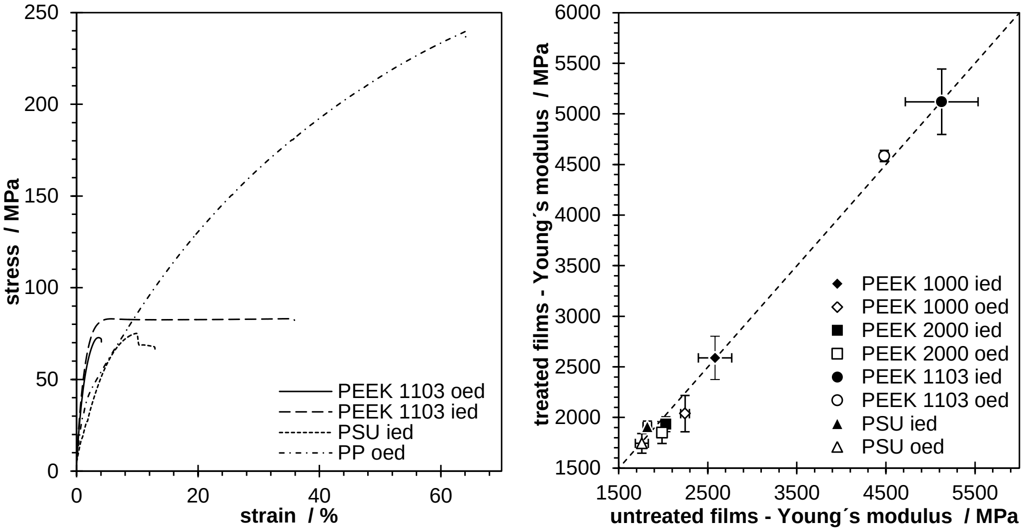

Figure 2: Stress-strain diagrams of selected polymer films (left) and parity plot showing the Young´s modulus for the physically treated polymer films (plasma and corona) vs. the untreated films (right) according to the direction of extrusion (ied: in extrusion direction, oed: orthogonal to extrusion direction)

Besides the small scale wetting optimization hydrodynamic considerations with respect to the apparatus geometry and process conditions show a strong dependence of temperature for the wetting hysteresis. Figure 3 shows the results for the stainless steel surface and the change of the minimum wetting rate both for increasing and decreasing liquid loads (left hand side). The right hand side of Figure 3 reveals that this effect is not only related to the changes of the physical properties of the process media induced by the temperature shift but also to the surface specific molecular interactions at the interface. The relationship between minimum wetting rate and temperature differs from a linear increasing to nonlinear decreasing tendencies for the polymers. It is obvious that some materials react more sensitive to the temperature induced activation of the functional groups or molecular interface than others.

The discussed effects of the surface treatments to the surface free energy affect the falling film hydrodynamics as well. Table 1 shows the results for the minimum wetting rate on a flat plane dependent on the different surfaces and its modifications. Due to the treatments the minimum wetting rate decreases for all surfaces. That effect implicates a more efficient heat exchange process. The untreated stainless steel surface is a technical grade surface with several scratches which results in a high deviation compared to the electro-polished modification. However, these results for the flat plane should be compared to wetting experiments with the spacer geometry used in the apparatus to quantify the influences both of hydrodynamic and surface energetic effects.

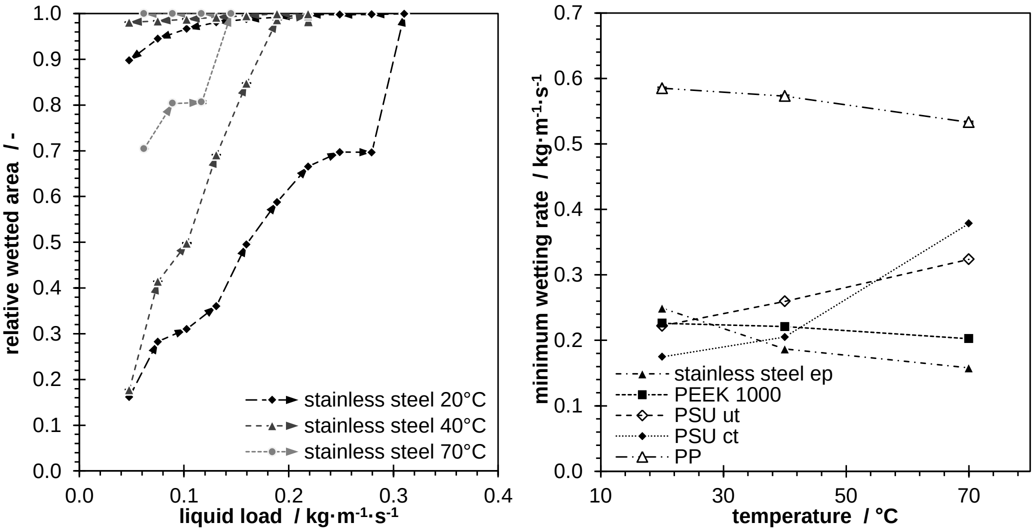

Figure 3: Wetting hysteresis with water for electro-polished stainless steel (left) and the minimum wetting rate for increasing liquid load and different surfaces (right) as a function of temperature, lab-scale wetting apparatus, flat surfaces, angle of inclination 90 °

Table 1: Minimum wetting rates in kg· m^{-1}·s^{-1} with water at 20 °C for treated and untreated surfaces

surface	untreated	treated	treatment
stainless steel	0.940 ± 0.004	0.249 ± 0.003	electro-polish
PEEK Aptiv® 1000	0.214 ± 0.009	0.198 ± 0.009	plasma treatment
PSU	0.222 ± 0.002	0.175 ± 0.001	corona treatment

4. Conclusions

Physical surface treatments of the studied surfaces showed a successful improvement of the surface free energy as well as the falling film wettability with water on a flat plate. However, the mechanical stability was not degraded. The impact of temperature on the wettability could be qualified for different surfaces. Further research is necessary to quantify the different scale contributions (surface energy, hydrodynamics) to the overall wettability improvement. Crystallisation fouling has to be studied besides the wettability under consideration of fluid dynamic apparatus optimization. Tensile tests with focus on other operational influences like temperature and process media in combination with further creep experiments should complete a mechanical database for the special interest of polymer film heat exchanger design.

Acknowledgment

The authors would like to thank the German Federal Ministry of Economics and Technology (BMWi) and the German Federation of Industrial Research Associations (AiF) for financially supporting the project (IGF-FV 16959 N).

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