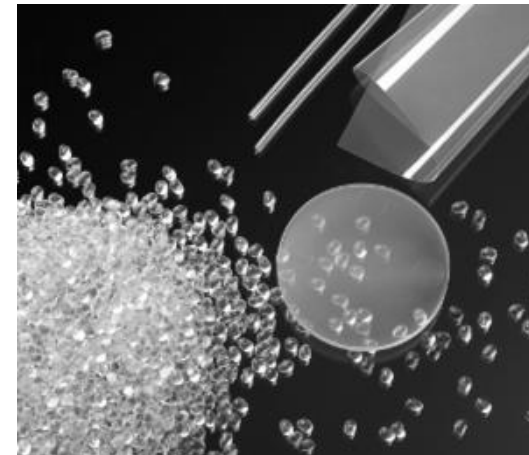


Conference Guide

3rd PhD-Workshop on Polymer Reaction Engineering

12th-14th September 2014 in San Sebastián



http://www.efce.info/PhD_Workshop+of+WPPRE.de

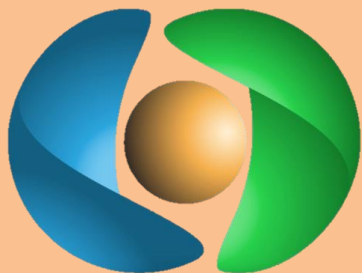


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sabic



Welcome to the 3rd PhD-Student Workshop on Polymer Reaction Engineering

Dear company representatives, professors and PhD-students,

The PhD-Student Workshop on Polymer Reaction Engineering represents an international platform where young researchers in the field of polymer reaction engineering can build up valuable networks. It is an opportunity to meet fellow PhD-students and to get into contact with interesting companies and potential employers. Moreover, PhD-students can benefit from useful feedback on their work and improve their soft skills by practicing the presentation of complex scientific topics.

The workshop is being held for the third time now and we would like to perpetuate it as an annual event. It has been launched in Lyon in 2012 with a total number of 35 participants. The second workshop has been organized in Hamburg last year and involved 43 people. This year we are recording a maximum number of registrations.

Just as the participant number is increasing from year to year we are also trying to continuously extend the scope of research fields covered in the oral presentations and poster contributions. This year you can look forward to contributions concerned with:

- bulk, emulsion, miniemulsion, gas phase and high pressure polymerization
- structure-property relations regarding heat transfer, wettability and coagulation phenomena and extrusion as well as adhesion behavior
- homopolymers, copolymers, blends, foams, nanogels and hybridpolymers

- packaging and biomedical applications
- results obtained by new analytical methods

Having all these wonderful topics up in our sleeves we are looking forward to an interesting workshop in San Sebastián with you.

The Organizing Committee

Organizing Committee

Markus Busch	Chair of WPPRE, TU Darmstadt
Werner Pauer	Secretary of WPPRE, University Hamburg
Jose R. Leiza	POLYMAT, University of the Basque Country
Claudia Schwartzkopff	TU Darmstadt
Amaia Agirre Iribarren	POLYMAT, University of the Basque Country
Ines Plaza	POLYMAT, University of the Basque Country

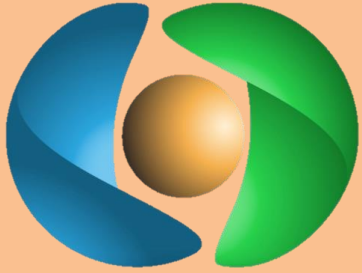
Sponsors



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Arrival in San Sebastián

Public Transport into the city & Your way to the workshop

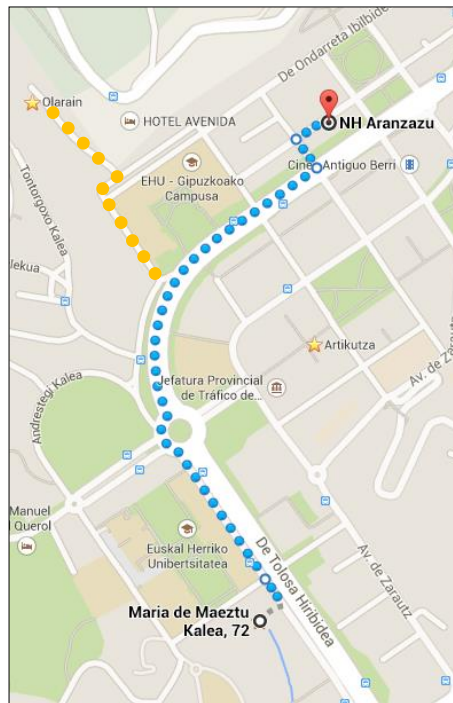
Transfer from the airport into the city

Once landed in Bilbao there is the possibility to take a bus to the city center of Donostia/San Sebastián. The bus PESA departs at the station 'Termibus' at the airport and takes between 1 hour and 1,5 hours for the transfer depending on the traffic. The final stop in San Sebastián is a central bus station (see the labels in the map on the right).

If you want to go to the Olarain residence or the NH Aranzazu, you should use the bus lines 24 or 27, which depart at the other side of the roundabout.

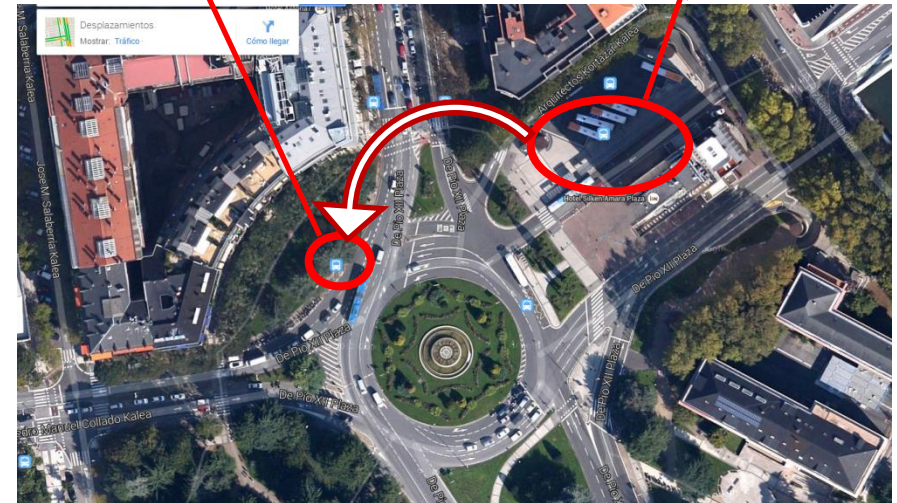
The way to the workshop

The Joxe Mari Korta Center, where the PhD-workshop is going to take place, is within a 10 minute walking distance from both hotels.



Bus lines to go to
OLARAIN and NH Aranzazu.
Bus stop: PIO XII

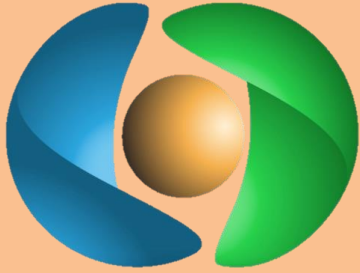
Central bus station
Final stop of airport bus



Contact

If you have any further questions, please feel free to contact us via email or visit our homepage.

wpre@chemie.tu-darmstadt.de
http://www.efce.info/PhD_Workshop+of+WPPRE.de



General Information

Language

The official language at the workshop is English.

Internet

You will be provided access to the wireless LAN in the POLYMAT when registering on Friday.

Insurance

The organizers do not accept responsibility for individual medical or personal insurance. Participants are strongly advised to take out their own insurance policies.

Telephone

The international code for Spain is +34.

Emergency phone numbers

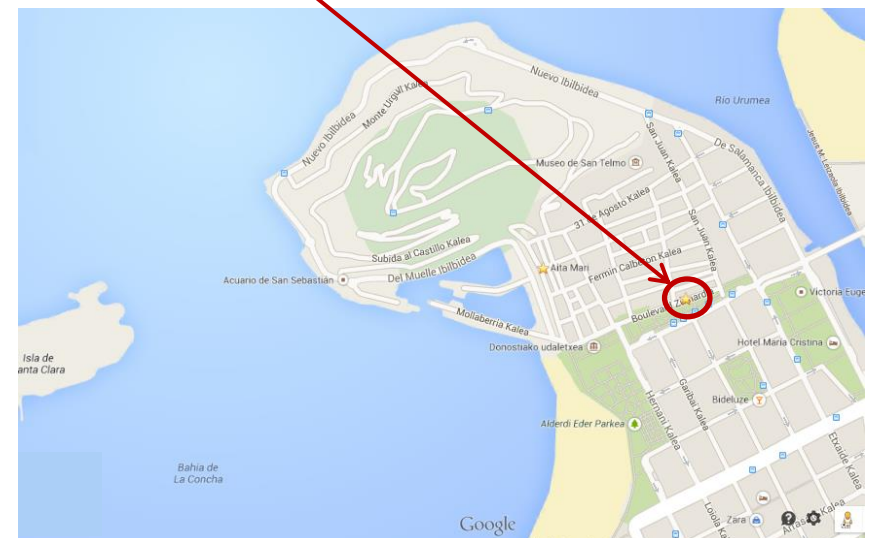
Police	092
Firebrigade	112
Ambulance	112

Taxi numbers

(+34) 943 46 46 46
(+34) 943-40 40 40

Tourist information

Boulevard, 8 (old town)
(+34) 943-481 166





Programme by days

Friday, 12th September 2014



POLYMAT



14:00 -14:45 **Registration at the conference site**
Poster wall preparation

14:45 -15:00 **Welcome**
Prof. Markus Busch, Prof. Jose R. Leiza

Session I

Chair: Amaia Agirre (University of the Basque Country, San Sebastián)

15:00 -15:20 **Paul Aigner** (Johannes-Kepler-University Linz)
Influence of Pre-Contacting on the Activity of a Ziegler-Natta Catalyst System

15:20 -15:40 **Leonhard Mayrhofer** (Johannes-Kepler-University, Linz)
Influence of Gas Velocity on the Particle Growth in Gas Phase PE Polymerization

15:40 -16:00 **Claudia Schwartzkopff** (Technical University Darmstadt)
Scanning Transitiometry – A Method to Investigate Phase Transitions and Thermodynamic Properties under High Pressures

16:00 -17:00 **Coffee Break and Poster Session**

Session II

Chair: Joana Kettner (Martin-Luther-University, Halle)

17:00 -17:20 **Barbara R. Lara** (C2P2 Lyon)
Reformulation of Acrylic Latexes for use in Flexible Food Packaging

17:20 -17:40 **Shaghayegh Hamzehlou** (University of the Basque Country)
Simulation of Polyurethan/Acrylic Hybrid Polymerization in Batch Miniemulsion Droplets



Programme by days

Friday, 12th September 2014



POLYMAT

17:40 -18:00 **Joseba Juaristi** (University of the Basque Country)
Morphology and Film Forming Properties of Acrylic Hybrid Emulsions

18:00 -18:20 **Ana B. López** (University of the Basque Country)
Waterborne Fluoropolymer Dispersions for Hydrophobic Coatings

18:30 -19:00 **Dr. L. Ivano Costa (SULZER)**
Process Technology at Sulzer Chemtech: from first concept to guaranteed plant performance

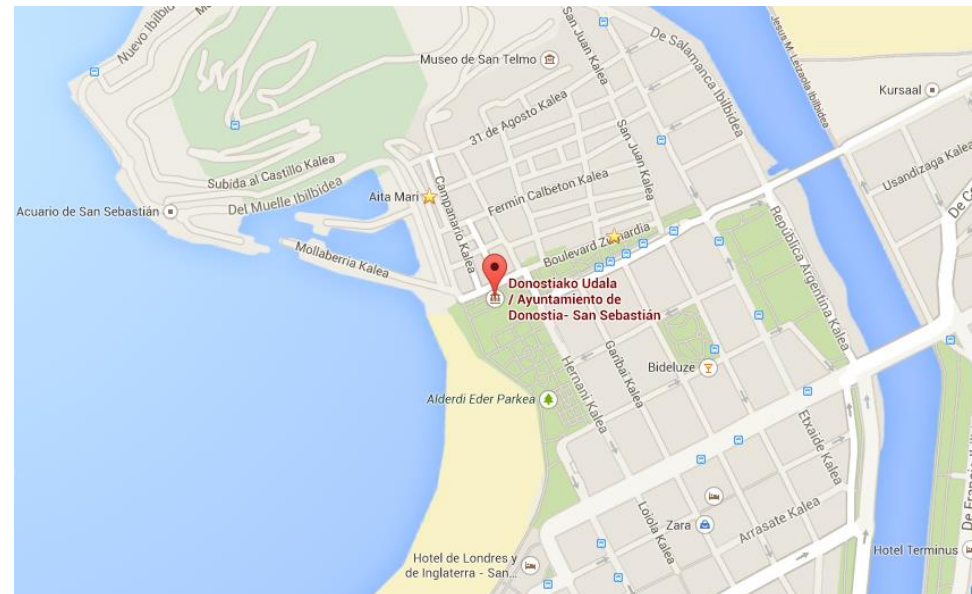
20:00 **Pintxos tour**
Meeting point: Town hall (ayuntamiento) in the old city of San Sebastián

kindly sponsored by:

SULZER

Pintxos...

literally means „spike“ and is a traditional snack, which is typically eaten in bars in the Basque country.





Programme by days

Saturday, 13th September 2014



POLYMAT

Session III

Chair: Claudia Schwartzkopff (Technical University Darmstadt)

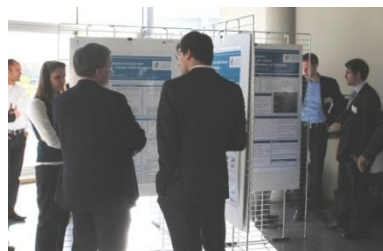
- 09:00 - 09:20 **Ana C. Méndez Ecoscia** (C2P2 Lyon)
Colloidal Stability of PVDF Latex Particles
- 09:20 - 09:40 **Martin Kroupa** (Institute of Chemical Technology Prague)
The Discrete Element Model of Shear-Induced Coagulation – the Structure of the Resulting Clusters
- 09:40 - 10:00 **Barthélémy Brunier** (CNRS-University of Lyon)
Analysis of the Effect of Laponite on Radical Exchange in Seeded Semibatch Pickering Emulsion Polymerization
- 10:00 - 10:20 **Judith van Wijk** (Eindhoven University of Technology)
Silica Microcapsules by Templating Pickering Emulsion Droplets: Mechanism of Formation

10:20 - 11:30

Coffee Break

and

Poster Session



Session IV

Chair: Martin Kroupa (Institute of Chemical Technology Prague)

- 11:30 - 11:50 **Leila Medeiros Santos** (C2P2 Lyon)
Monitoring of Miniemulsion Polymerization of the Methyl Methacrylate in the Presence of Ionic Liquids using Near Infrared Spectroscopy
- 11:50 - 12:10 **Sevilay Bilgin** (University of the Basque Country)
Stabilization of Emulsions by Using Ionic Monomers
- 12:10 - 12:40 **Dr. Eric Grolman** (DSM)
Working on Polymer Reaction Engineering in DSM's Material Sciences cluster

13:00

Lunch at the bar Artikutza, which is in walking distance
(Oihenart street, 3)

kindly sponsored by





Programme by days

Saturday, 13th September 2014



POLYMAT

Session V

Chair: Andres F. Sierra Salazar (ENSCM, Montpellier)

- 14:20 - 14:40 **Alejandro Arzac** (University of the Basque Country)
Reduced Graphene Oxide/Polymer Composites Latexes by Emulsion and Miniemulsion polymerization
- 14:40- 15:00 **Alicia De San Luis** (University of the Basque Country)
Nanostructured Polymeric Aqueous Dispersions containing Quantum Dots
- 15:00- 15:20 **Gordana Siljanovska Petreska** (University of the Basque Country)
SERS Active Substrates based on Ag/Graphene/Polymer obtained by Laser Ablation using Rh6G as a Model Compound
- 15:20 - 15:40 **Aintzane Pikabea** (University of the Basque Country)
Dual Stimuli-Responsive Nanogels: Promising Nanocarriers for Controlled Drug Delivery

15:40 - 16:30 **Coffee Break and Poster Session**

- 16:30-17:00 **Dr. Wolfgang Gerlinger (BASF)**
Polymer Reaction Engineering in BASF

Session VI

Chair: Barbara Rezende Lara (C2P2, Lyon)

- 17:00 - 17:20 **Pavel Ferkl** (Institute of Chemical Technology Prague)
Heat transfer Phenomena in Micro- and Nanocellular Foams
- 17:20- 17:40 **Joana Kettner** (Martin-Luther-University, Halle)
Kinetic Study of the Bulk Polymerization of Propylene with Metallocene Catalyst using Reaction Calorimetry
- 17:40 - 18:00 **Arkom Drawpateep** (Martin-Luther-University, Halle)
High Impact Polypropylene Process Review and Future Trend in Research
- 18:00 - 18:20 **Miguel Plata** (Martin-Luther-University, Halle)
Experimental Setup for Heterophasic Propylene Copolymers

18:20-19:00 **Refreshments and Poster Session**



Programme by days

Saturday, 13th + Sunday, 14th



POLYMAT

20:30

Dinner at the restaurant Aita Mari
(Puerto street, 23)

kindly sponsored by



Sunday, 14th

11:00 **Guided tour through the old town of San Sebastián**

Meeting point: Town hall (ayuntamiento) in the old city
of San Sebastián



13:30 **Lunch at the hotel Eceiza with the award for the best contribution**

Satrustegi street, 13
(Ondarreta beach)

Lunch & tour kindly sponsored by



The prize for the best contribution
is kindly sponsored by

WILEY



Places to know



POLYMAT

POLYMAT Institute



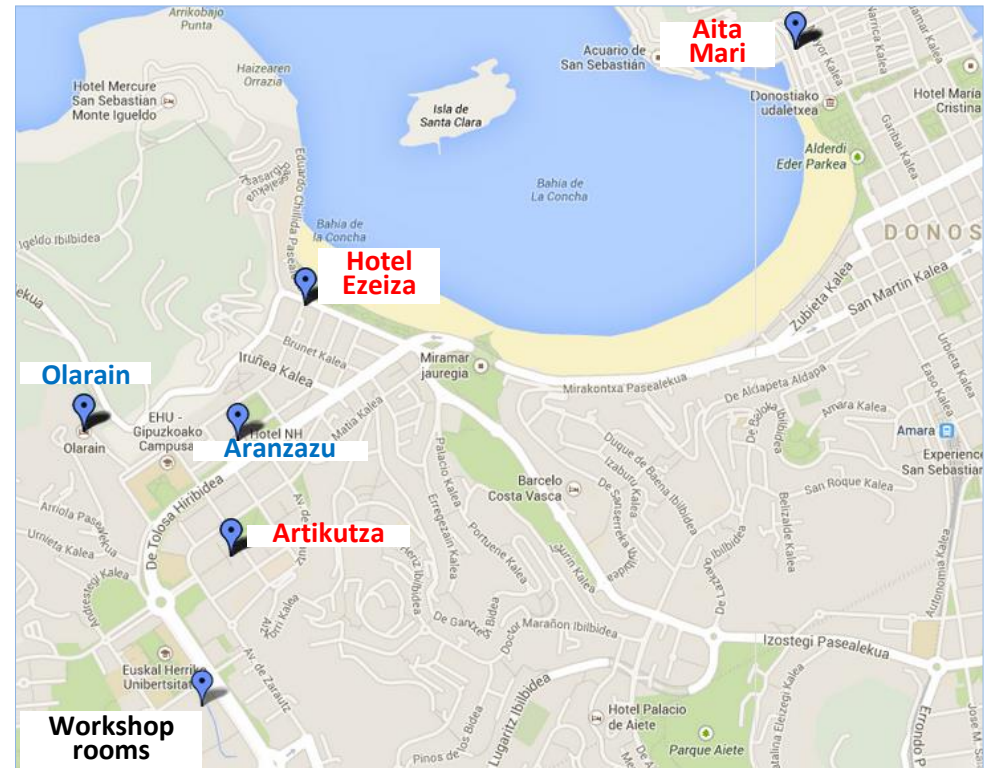
**Joxe Mari Korta
Center**

Avda. Tolosa, 72
20018 Donostia
- San Sebastian
SPAIN



San Sebastián Overview

- Hotels
- Restaurants
- Workshop rooms





List of posters

- P. Ferkl, R. Pokorny, J. Kosek**
Polymeric Foams: Morphology and Heat Transfer
- A. Gapchenko, H.-U. Moritz, W. Pauer**
High-Temperature Emulsion Polymerization of Styrene and n-Butyl Acrylate
- M. Balyschewa, M. Busch**
Cloud Point Pressure Curves of High Density Ethylene Acrylate Copolymers
- A.B.López, J.C. de la Cal, J.M. Asua**
Waterborne Fluoropolymer Dispersions for Hydrophobic Coatings
- J. Juaristi, P.-E. Dufils, A. Veneroni, Y. Vanderveken, J. M. Asua**
Morphology and Film Forming Properties of Acrylic Hybrid Coatings
- B. Brunier (CANCELLED)**
Evaluation of Laponite® Partitioning in Pickering Emulsion Polymerization
- A. C. Méndez-Ecoscia, M. Fonseca-Marques, T.F.L McKenna, N. Othman**
Colloidal Stability of PVDF Latex Particles
- L. Medeiros Santos, M. J. Amaral, M. Fortuny, C. Dariva, E. Franceschi, A. F. Santos, T. F.L. McKenna**
Monitoring of Miniemulsion Polymerization of the Methyl Methacrylate in the Presence of Ionic Liquids using Near Infrared Spectroscopy
- A. Pikabea, J. Ramos, J. Forcada**
PH- and T-responsive nanogels: potentially useful vehicles in controlled drug release
- M. Madani, H.- U. Moritz, W. Pauer**
Fouling in a Batch Reactor during an Emulsion Polymerization
- N. Monien, W. Pauer, H.-U. Moritz, C. Scholten, E. Alsaffar**
Swelling Capability of Hydrophilically Modified Polyurethane Polymers
- K. Rossow, F. G. Lueth, W. Pauer, H.-U. Moritz**
Process Intensification through Smart Scale Technology in Continuous Emulsion Polymerization
- P.Aigner, C. Paulik, A. Krallis**
Influence of Pre-Contacting on the Activity of a Ziegler Natta Catalyst in a 0.5 L Polymerization System
- A. Drawpateep, T. Kroener, M. Bartke**
Kinetics of Copolymerization of Acrylamide and MADAMBQ



List of posters



POLYMAT

15. **C. W. Nörnberg, B.Schroeter, W. Pauer, H.-U. Moritz, W.-D. Hergeth**
Continuous Emulsion Copolymerization of Vinyl Acetate in a Laminar Stirred Tube Reactor (LSTR)
16. **M. Kroupa, M. Vonka, J. Kosek**
Shear-induced Coagulation in Colloidal Dispersions - Modeling by Discrete Element Method
17. **B. R. Lara, T.F.L. McKenna, K. Ouzineb**
Reformulation of Acrylic Latexes for use in Flexible Food Packaging
18. **A. De San Luis, A. Bonnefond, M. Paulis, J.R. Leiza**
Nanostructured Polymeric Aqueous Dispersions containing Quantum Dots
19. **M. Öppling, M. Busch**
Influence of various Agents on the Radical High Pressure and High Temperature Ethylene Polymerization
20. **L. Mayrhofer, C. Paulik**
Single Particle Gas-Phase Ethylene Homo-Polymerization with Ziegler-Natta Catalyst



Abstracts of all participants



POLYMAT

1. Paul Aigner
2. Leonhard Mayrhofer
3. Claudia Schwartzkopff
4. Bárbara Rezende Lara
5. Shaghayegh Hamzehlou
6. Joseba Juaristi
7. Ana Belén López González
8. Ana Carolina Méndez-Ecoscia
9. Martin Kroupa
10. Barthélémy Brunier (*CANCELLED*)
11. Judith van Wijk
12. Leila Medeiros Santos
13. Sevilay Bilgin
14. Alejandro Arzac
15. Alicia De San Luis
16. Gordana Siljanovska Petreska
17. Aintzane Pikabea
18. Pavel Ferkl
19. Joana Kettner
20. Arkom Drawpateep
21. Miguel Plata
22. Mania Madani
23. Nicole Monien
24. Kristina Rossow
25. Christian Werner Nörnberg
26. Margarita Balyschewa
27. Alisa Gapchenko
28. Maria Öppling

Influence of Pre-Contacting on the Activity of a Ziegler-Natta Catalyst System

Paul Aigner, Institute for Chemical Technology of Organic Materials (CTO), Johannes Kepler University, Austria;

C. Paulik, Institute for Chemical Technology of Organic Materials (CTO), Johannes Kepler University, Austria;

A. Krallis, Borealis Polymers Oy, Finland

INTRODUCTION

Polyolefines account for about one third of the Plastics production [1]. For the production of Polyolefines heterogeneous Ziegler-Natta based catalysts dominate the market. There is a constant progress in catalyst design to increase the catalyst activity [2]. To reach the maximum potential of a catalyst system several steps prior the main polymerization process need to be done. It has been shown that pre-polymerization and pre-contacting can increase the activity of catalyst system dramatically [3,4]. The catalyst system usually consists out of a TiCl₃ based component and an aluminium-alkyl. Out of these two components an active center as shown in Figure 1 is formed, which is required to perform the polymerization process. The formation of the active center has a big influence on the catalyst productivity.

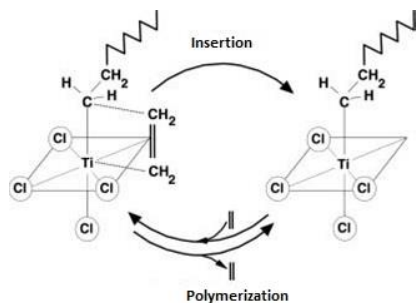


Figure 1: Active center and polymerization scheme [5].

PRACTICAL PROCEDURE

Therefore a more detailed investigation has been performed to study the relation between activity and pre-contacting of a Ziegler-Natta catalyst system for polyethylene. In addition the polymer powder properties such as crystallinity, molecular weight and particle morphology have been analyzed as well. The experiments have been performed in 0.5 l multi-purpose reactor system in slurry. Triethylaluminium (TEA) has been used as co-catalyst. Of special interest has been the influence of the pre-contacting duration on the catalyst activity. For that reason the pre-contacting time has been varied. The polymerization time has been one hour at 85 °C. Furthermore the catalyst behavior when copolymerizing ethylene with other α -olefins has been looked at.

RESULTS

The investigation reveals an optimum pre-contacting time. There is a linear increase of the activity till the maximum and afterwards it decreases again. At the optimum pre-contacting the activity increases by 25 % compared without pre-contacting. Beyond the optimal pre-contacting time it nearly decreases to the starting value again. The activation via pre-contacting is heavily dependent on the catalyst and the conditions, but with just the right timing, pre-contacting can increase the productivity by one quarter.

REFERENCES

- 1) PlasticsEurope, (2013), Plastics - The Facts 2013, <http://www.plasticseurope.org/cust/documentrequest.aspx?DocID=59108>, accessed on: 2/7/2014.
- 2) Galli P., Vecellio G., Technology: driving force behind innovation and growth of polyolefins, *Progress in Polymer Science*, (2001), 26(8), 1287–1336.
- 3) Daftaribesheli M., Comparison of catalytic ethylene polymerization in slurry and gas phase, (2009), University of Twente [Host], Enschede.
- 4) McKenna, Timothy F. L., Tioni E., Ranieri M. M., Alizadeh A., Boisson C., Monteil V., Catalytic olefin polymerisation at short times: Studies using specially adapted reactors, *Can. J. Chem. Eng.*, (2013), 91(4), 669–686.
- 5) Böhm L. L., The ethylene polymerization with Ziegler catalysts: fifty years after the discovery, *Angew. Chem. Int. Ed. Engl.*, (2003), 42(41), 5010–5030.

Your notes:

Influence of Gas Velocity on the Particle Growth in Gas Phase PE Polymerization

*Leonhard Mayrhofer, Kompetenzzentrum Holz GmbH, Altenbergerstraße 69, 4040 Linz, Austria;
C. Paulik, JKU Linz, Institut für Chemische Technologie Organischer Stoffe, Altenbergerstraße 69,
4040 Linz, Austria;*

A. Krallis, Borealis Polymers Oy, P.O. Box 330, FI-06101 Porvoo, Finland

In this work a comparison of overflow / no- overflow gas phase experiments is shown. An industrial Ziegler-Natta (ZN)- catalyst system is used for ethene in a 7 mL micro-gasphase reactor. The ZN catalyst system is based on Ti (2.3 %) supported on a $MgCl_2/SiO_2$ carrier. All manipulations with the catalyst were performed in a glovebox. Conditions for the gas phase polymerizations were: 20 bar of ethene pressure, different reactor temperatures (40 °C, 50 °C, 70 °C and 85 °C) and an Al/Ti ratio of 25, while Triethylaluminium (TEA) acted as cocatalyst and scavenger for all polymerizations.^[1] Overflow conditions were 14 mL per minute which corresponds to a volume exchange of two times per minute. With video microscopy (Carl Zeiss AxioTech Vario 25 HD equipped with a U series digital camera) the growth of the particles was observed and 20 spherical particles were chosen for the calculation of the rate of polymerization. To receive information regarding the surface of the grown polymer, scanning electron microscopy was used.

In this work two different reactor setups are directly compared while the only difference is the overflow condition. It was shown, that with overflow less growth for the temperatures 40 °C, 50 °C and 70 °C can be observed. At 85 °C a slightly higher polymerization rate is detectable. Handling the heat of polymerization of growing olefin particles is an important field for industry and academia and this work allows deeper understanding of the PE gas phase polymerization process.

REFERENCES

- 1) L. Mayrhofer, C. Paulik, *Macromol. React. Eng.*, **2014**, *8*, 194.

Your notes:

Morphology and Film Forming Properties of Acrylic Hybrid Emulsions

Joseba Juaristi, J. M. Asua

POLYMAT, University of the Basque Country UPV/EHU, 20018 Donostia-San Sebastián, Spain

Waterborne coatings have attracted a lot of interest in the last years, as a sustainable alternative to the use of solvent based coatings. The advantages in the use of such a kind of product are to be found in the limitation in the use of VOCs (volatile organic compounds) and in the possibility of application at room temperature. These coatings can also reduce the amount of hazardous waste generated, depending on the type of paint used. Waterborne coatings may benefit from the presence of domains with either high T_g or crystallinity.^{1,2} These coatings often present resistance to different agents and/or good barrier properties.³ In order to optimize the properties an adequate balance between the hard polymer and the soft film-forming polymer should be achieved. A possibility is a blend of dispersion of hard polymer and acrylic resins using seeded emulsion copolymerization.⁴ However, phase separation often occurs upon film formation leading to poor application properties. Incorporation of both hard and soft phases in the same particle would minimize this effect. In the implementation of this idea there are plenty of open questions regarding aspects as particle morphology, fractions of soft and hard phases and degree of interpenetration among the phases.

This work is an attempt to clarify some of these open questions. In particular, using a core-shell morphology with the soft polymer in the shell, which was considered to be the most promising morphology, the effect of the fractions of soft and hard phases and degree of interpenetration among the phases on film formation was investigated.

The core-shell particles were synthesized in a two-step process. In the first step, a densely crosslinked particle was formed by semicontinuous emulsion copolymerization of styrene and divinylbenzene. The shell was formed in a seeded semicontinuous emulsion copolymerization process, using the particles produced in the first stage as a seed. The composition of the shell was varied and copolymers of styrene/butyl acrylate and methyl methacrylate/butyl acrylate were used. The composition of the shell was adjusted to have a low enough T_g. In some cases a super-spreader was added to facilitate film formation of solids surfaces by decreasing the surface tension of the latex.

The results in Table 1 show that the fraction of soft copolymer has a strong effect on film properties. Taking into account that the maximum volume fraction for monodispersed packed spheres is 64%, one would expect to have continuous film of soft polymer for shell contents in the range of 36-40%. However, Table 1 shows that a substantially higher fraction is needed to achieve the MFFT characteristic of the polymer in the shell. This strongly suggests that there is some interpenetration between the soft shell and the hard core that resulted in a lower fraction of soft shell useful to form film.

Shell (%)	22	27	36	45	55	65
MFFT (°C)	>90	>90	85	58	21	13

Table 1: Values of minimum film formation temperature (MFFT) for p(St/DVB)/p(MMA/BA) systems.

TEM analysis of the samples reveals that the particles had a core-shell morphology and the acrylic rich copolymer (clear polymer in the TEM picture) was mainly located in the shell. However, the thickness of the shell is too thick for the fraction of the copolymer used. This further supports the idea that there is a penetration of the soft polymer in the core.

The research reveals that the incorporation of small amounts of low-T_g polymer into a high-T_g crosslinked core can substantially improve the film forming properties of the coatings. However, penetration of the low T_g polymer in the core needs to be avoided in order to optimize the amount of acrylic polymer in the formulation.

REFERENCES

- 1) Patent No. 5,783,632
- 2) Patent No. 5,612,415
- 3) F. Bückman, A. Overbeek, T. Nabuurs, (2001). Self Crosslinking Surfactant Free Acrylic Dispersions for High Performance Coatings Applications. *European Coatings Journal*, 53, pp.1-8
- 4) Helmiyati, Budianto, E. (2008). Emulsion Polymers of Core-Shell Styrene-Butyl Acrylate: The Effect of Feeding and Aging Time on Particle Size Distribution. *Journal of Physical Science*, 19(2). pp. 117-125

Your notes:

(CANCELLED)

Analysis of the effect of Laponite® on Radical exchange in seeded semibatch Pickering Emulsion Polymerization

*Barthélémy Brunier, Y. Chevalier, N. Sheibat-Othman, LAGEP / CNRS-University of Lyon, France
E. Bourgeat-Lami, C2P2, LCPP group / CNRS-University of Lyon, France*

"Pickering" stabilization of latex particles has recently emerged as a new method to create nanocomposite colloids by adsorption of solid particles at solid latex interfaces^[1] and is named "Emulsion polymerization" by analogy to solid-stabilized emulsions^[2]. The elaboration of composite latexes allows combining attributes of inorganic solids with the processing and handling advantages of organic polymers which allows for instance to improve mechanical and water-resistance properties in waterborne organic coatings^[3].

The stabilization of polymer latex particles elaborated by Pickering polymerization mainly takes place by steric repulsions between adsorbed inorganic solid particles. The later form a rigid mechanical barrier that prevents the polymer latexes from coalescing. Electrostatic phenomena do not significantly contribute to the colloidal stability. However, the presence of inorganic particles at the surface of polymer particles might affect radical adsorption and desorption due to their charges or to the mechanical barrier. Therefore the growth step during the polymerization may be affected by the presence of inorganic particles.

In this work, we investigate the effect of Laponite® clays concentration on radical exchange, and therefore particle growth, in emulsion polymerization of styrene, in the absence of surfactant or other additives. Both experimental and modelling investigations are handled.

Seeded experiments were realized by varying the amount of Laponite®. The used seed was produced at 70°C using potassium persulfate as initiator in presence of a small amount of Laponite® (for nucleation and stabilization). The seeded experiments start in interval III, eliminating therefore the nucleation phase. Experiments presenting coagulation were also eliminated, to ensure constant particle number. The focus can therefore be made on particle growth and more precisely radical entry (absorption) and exit (desorption) from the latex particles. Experimental estimation of the average number of radicals per particle demonstrates that radical exchange plays an important role in Pickering emulsion polymerization. However, the Laponite® concentration does not seem to affect the growth rate.

In parallel, the effect of Laponite® concentration on particle growth was investigated by modelling, which allows estimation of adsorption and desorption parameters that are not available in the literature. Smith and Ewart [4] first described the transfer of free radical activity into the interior of a polymer particle by direct diffusion of a free radical into a polymer particle:

$$R_c^p = 4\pi \cdot r_p \cdot D_w [R^w] \cdot N_p = k_c^p \cdot [R^w] \cdot N_p$$

However, the diffusion theory only applies accurately to large uncharged particles. In order to apply this theory to smaller and charged particles, two additional phenomena must be considered: reversible absorption and electrostatic repulsion. For instance, free radical diffusion might be hindered due to the presence of anionic clay platelets on the surface of latex particles. With this modification, to be considered absorbed by the particles, a radical must propagate or terminate before eventual desorption. This is done by incorporating an efficiency absorption factor in the absorption equation (see Hansen and Ugelstad [5] [6] [7]). The net rate of radical absorption by a particle can be obtained from the following expression, accounting for the theory of mass transfer and the "absorption efficiency factor" F_p :

$$k_c^p = 4\pi \cdot r_p \cdot D_w \cdot \bar{F}_p$$

Hansen and Ugelstad [7] also proposed an equation that combines the electrostatic repulsion factor, with capture reversibility to obtain the expression of F_p . Using this model, the electrostatic repulsion factor was estimated with varying Laponite® concentration in a way to fit experimental data. This again confirms that the Laponite® concentration does not affect the growth rate.

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Your notes:

Kinetic Study of the Bulk Polymerization of Propylene with Metallocene Catalyst using Reaction Calorimetry

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In comparison to the gas-phase or slurry polymerization, the kinetics of the polymerizations carried out in bulk phase are more difficult to investigate. In gas-phase or slurry processes, kinetic information are accessible by semi-batch operation of the reactor: In batch operation with increasing conversion, the pressure would drop; in semi-batch operation this pressure drop is compensated by feeding of monomer controlled by a pressure control loop. As long as isothermal conditions are met and external mass-transfer restrictions are avoided, the fed amount of monomer corresponds to the monomer consumption and is proportional to reaction rate.

In case of the bulk polymerization, the reactor pressure in principle always corresponds to the vapor pressure of liquid propylene, which is constant with conversion. The semi-batch approach outlined above is therefore not applicable. Furthermore, the monomer concentration in the reactor is higher leading to higher polymerization rates compared to slurry- or gas-phase polymerization.

In literature, only a few references about online-measurement of bulk phase polymerization can be found using either reaction calorimetry^{1,2,3} or dilatometry^{4,5}.

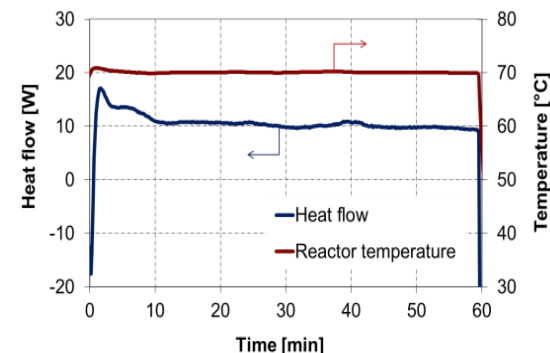
In this study a reaction calorimeter from ChemiSens[®] was used, which is based on the principle of the heat flow calorimetry. The main advantage of this special calorimeter is that the heat flow can be measured independent of the heat transfer conditions and filling level in the reactor. The heat flow is measured via the heat conductivity in the reactor base. No calibration is needed.

The reaction kinetics can be directly determined from the generated chemical heat of the reaction, because it is direct proportional to the reaction rate. The heat input of the stirrer is measured by means of a torque transducer.

The purpose of the study is the kinetic investigation of the bulk phase polymerization of propylene with a supported metallocene catalyst. Main approach is to investigate the influence of different reaction conditions (reaction temperature, hydrogen concentration) on activity and to determine the kinetics of the catalyst.

Two different polymerization procedures were investigated: polymerization with non-isothermal prepolymerization and polymerization with prepolymerized catalyst. In the first procedure, the prepolymerization starts with the injection of the catalyst at mild conditions. During the prepolymerization, the reactor temperature is increased until the desired reaction

reached and the main polymerization starts. In the second procedure, the prepolymerized catalyst is firstly produced at milder reaction conditions and stored under inert conditions. In the main polymerization, the prepolymerized catalyst is directly injected under reaction conditions.



$$\rightarrow \dot{Q}_{Chem} = rate \cdot (-\Delta H_R) = \dot{Q}_{HF} - P_{stirr}$$

The results from polymerizations carried out at same reaction conditions show that the reached activities are comparable for both processes. Nevertheless, the main advantages of the second procedure are: no undefined heating up-periods during prepolymerization, degree of prepolymerization is known, kinetic profiles are earlier accessible because isothermal conditions are reached faster.

The presented study therefore focuses on the polymerization with prepolymerized catalyst. The influences of reaction temperature in the main polymerization and the amount of hydrogen on the activity are investigated. Furthermore, prepolymers with different degree of polymerization were prepared in order to investigate the influence of DP on activity in the main polymerization process.

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Your notes:

High Impact Polypropylene Process Review and Future Trend in Research

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Having versatile properties and wide range of applications, plastic plays a vital role in our daily life. In 2012, 288 tons of plastic has been produced around the world. One among the most pronounced plastic regarding its consumption is polypropylene (18.8%). After the first discovery of isotactic polypropylene by G. Natta et al. in 1954, polypropylene has shown a significantly improvement in term of product properties. One major direction in polypropylene development is to extend its application at low temperature, since isotactic polypropylene glass transition temperature (T_g) is around 0°C. In order to extend polypropylene application in sub-zero temperature environment, the so called high impact polypropylene was developed.

The high impact polypropylene consists of isotactic polypropylene matrix and finely dispersed elastomeric phase. Originally achieve by compounding isotactic polypropylene and elastomeric material likes ethylene-propylene rubbers (EPR) or ethylene-propylene diene elastomers (EPDM). Later on the catalyst development and process technology improvement had driven the production of high impact polypropylene to in-reactor design. The driving force was not only energy saving by elimination of compounding step, but the resin produced in reactor offers better particles morphology and performance.

Nowadays, production of high impact polypropylene is achieved by using two stages in series process. In the first stage, isotactic polypropylene continuous phase matrix is produced in liquid or gas phase process. In the second stage, elastomeric phase of ethylene-propylene copolymer is formed into the former isotactic polypropylene particle to enhance homogeneously dispersion of elastomeric phase. Number of industrial process were developed and used to produce high impact polypropylene including Spheripol, Spherizone, Catalloy process (Lyondell Basell), Borstar (Borealis), Unipol process (Dow Chemicals), Hypol II (Mitsui Chemicals), Novolen process (Lumus Novolen Technology), Amoco process (Ineos), vertical stirred-bed gas phase process (BASF).

The process most widely used for commercial PP production is the Spheripol process by Lyondell Basell. Lyondell Basell claims that the process has over 100 licensed lines around the world, with more than 20 million tones capacity. Spheripol is a hybrid process consists of two loop reactors and fluidized bed reactor connected in series. The homopolymerization to form isotactic polypropylene continuous phase matrix is conducted in the bulk phase loop reactors. The typical operating conditions in bulk polymerization are 50 - 80°C, 20 – 40 bar. The benefits of using this loop reactor cascade are: high specific cooling surface, excellent heat and mass transfer condition, narrow residence time distribution, full use of reactor volume, and less investment cost. It has been widely regards as the most important technology to produce homopolypropylene.

In the second stage, elastomer phase is produced in gas phase fluidized bed reactor. The heterophasic copolymer with up to 25 wt% ethylene content is formed. This copolymerization step is performed in gas phase polymerization, to avoid dissolution of the amorphous copolymer in liquid propylene. The general operating conditions in gas phase polymerization are 50 - 80°C, and 10 – 20 bar.

The research and development in high impact polypropylene is continuing in all areas including production process, catalyst and product development. In term of product, the challenges are on improving stiffness, toughness, transparency, and processability. Incorporating more than one disperse phase to enhance toughness of the product is also being interests. The catalyst development is moving toward single site catalyst, while development in Ziegler-Natta catalyst is still focus on the support size, internal and external donors and control of the different kind of active sites. The concept of hybrid catalyst system could also be an option for producing wider range of high impact polypropylene. Regarding legal regulation the development phthalate free catalyst system will soon become essential. In process development, recently multi-zone circulating reactor received highly interests. The continuous multi-stage polymerization offers short residence time for particle to circulate between two phase of polymerization, resulting highly uniform copolymer component dispersion.

Your notes:
