

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

WILEY SULZER







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	cretary 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





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.





Contact

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

> wppre@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







Friday, 12th September 2014



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

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

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



20:00

Programme by days



Friday, 12th September 2014

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

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Pintxos...

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









Saturday, 13th September 2014

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



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 usind Near Infrared Spectroscopy

Session IV

- 11:50 12:10Sevilay 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)



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Saturday, 13th September 2014

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 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





POLYMAT

Saturday, 13th + Sunday, 14th

20:30

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



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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





Places to know



POLYMAT

POLYMAT Institute



Joxe Mari Korta Center

Avda. Tolosa, 72 20018 Donostia - San Sebastian SPAIN







List of posters



POLYMAT

- 1. <u>P. Ferkl</u>, R. Pokorny, J. Kosek Polymeric Foams: Morphology and Heat Transfer
- <u>A. Gapchenko</u>, H.-U. Moritz, W. Pauer
 High-Temperature Emulsion Polymerization of Styrene and n-Butyl Acrylate
- 3. <u>M. Balyschewa</u>, M. Busch

Cloud Point Pressure Curves of High Density Ethylene Acrylate Copolymers

4. A.B.López, J.C. de la Cal, J.M. Asua

Waterborne Fluoropolymer Dispersions for Hydrophobic Coatings

- 5. <u>J. Juaristi</u>, P.-E. Dufils, A. Veneroni, Y. Vanderveken, J. M. Asua Morphology and Film Forming Properties of Acrylic Hybrid Coatings
- 6. <u>B. Brunier</u> (CANCELLED) Evaluation of Laponite[®] Partitioning in Pickering Emulsion

Polymerization

7. <u>A. C. Méndez-Ecoscia</u>, 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 Mathacrylate in the Presence of Ionic Liquids using Near Infrared Spectroscopy
- <u>A. Pikabea</u>, J. Ramos, J. Forcada
 PH- and T-responsive nanogels: potentially useful vehicles in controlled drug release
- **10.** <u>M. Madani</u>, H.- U. Moritz, W. Pauer Fouling in a Batch Reactor during an Emulsion Polymerization

- 11. <u>N. Monien</u>, W. Pauer, H.-U. Moritz, C. Scholten, E. Alsaffar Swelling Capability of Hydrophilically Modified Polyurethane Polymers
- **12.** <u>K. Rossow</u>, F. G. Lueth, W. Pauer, H.-U. Moritz Process Intensification through Smart Scale Technology in Continuous Emulsion Polymerization

13. <u>P.Aigner</u>, C. Paulik, A. Krallis

Influence of Pre-Contacting on the Activity of a Ziegler Natta Catalyst in a 0.5 L Polymerization System

14. <u>A. Drawpateep</u>, T. Kroener, M. Bartke

Kinetics of Copolymerization of Acrylamide and MADAMBQ



List of posters





15. <u>C. W. Nörnberg</u>, B.Schroeter, W. Pauer, H.-U. Moritz, W.-D. Hergeth

Continuous Emulsion Copolymerization of Vinyl Acetate in a Laminar Stirred Tube Reactor (LSTR)

- 16. <u>M. Kroupa</u>, M. Vonka, J. Kosek Shear-induced Coagulation in Colloidal Dispersions - Modeling by Discrete Element Method
- 17. <u>B. R. Lara</u>, T.F.L. McKenna, K. Ouzineb Reformulation of Acrylic Latexes for use in Flexible Food Packaging
- 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





- 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

 <u>Paul Aigner</u>, 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 TiCl 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 I 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

- 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.
- Daftaribesheli M., Comparison of catalytic ethylene polymerization in slurry and gas phase, (2009), University of Twente [Host], Enschede.
- 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.

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

Your notes:

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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 MgCl₂/ SiO₂ 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.

Scanning Transitiometry – A Method to Investigate Phase Transitions and Thermodynamic Properties under High Pressure

<u>Claudia Schwartzkopff</u>, Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Germany; M. Busch, Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Germany

Nowadays heat integration is a crucial task in the development and optimization of chemical processes and contributes non-negligibly to their profitability. However, before dealing with the energy efficiency of a system, information on the thermodynamic properties of the involved substances at process conditions is needed. In most cases reliable data sets including miscibilities and the associated enthalpies of mixing as well as heat capacities for the main components are already available from different databases. Elsewise those quantities can be measured in a straightforward manner by means of standard analytical techniques, which have been approved for ambient and low pressures.

In the field of polyolefines the measurement of thermodynamic properties is in fact more delicate since one may encounter process pressures of up to 3000 bar such as in the LDPE production. Moreover these high pressures are accompanied by high temperatures of 200-300 °C. Such extreme conditions complicate the determination of thermodynamic data because of the conflicting requirements of high sensitivities on the one hand and pressure-tight design of the sample vessels on the other hand. In order to overcome this contradiction several concepts have been developed.

One idea for the investigation of polymer miscibility with low molecular fluids under high pressures and temperatures is the use of autoclaves with a transparent sapphire window, so called visual cells. With the latter cloud points are determined by visual observation of the polymer precipitation. However, the results of these measurements can vary depending on the operator and the derivation of reliable quantitative information on solubility is difficult if not impossible. [1]

In comparison to the visual cell scanning transitiometry represents a more sophisticated method to examine miscibilities and other thermodynamic properties under high pressures. [2] This rather unknown technique is introduced and its advantages are discussed. The calibration procedure is outlined and the reproducibility of the measurements reviewed. The first experiments employing scanning transitiometry in our group are presented showing the effects pressurizing media on melting and crystallization of a low density PE polymer under ambient to medium pressures. An outlook on future applications of scanning transitiometry for the determination of enthalpies of mixing and heat capacities under high pressures up to 2500 bar is given.

REFERENCES

- 1) R. Dohrn, J.M.S. Fonseca, S. Peper, Experimental methods for phase equilibria at high pressures, *Annual Review of Chemical and Biomolecular Engineering*, 3, 343, 2012.
- 2) S. L. Randzio, Ch. Stachowiak, J.-P.-E. Grolier, Transitiometric determination of the threephase curve in asymmetric binary systems, *J. Chem. Thermodyn.*, 35, 639, 2003.

Acknowledgments:

Claudia Schwartzkopff gratefully acknowledges her scholarship funded by the Merck'sche Gesellschaft für Kunst und Wissenschaft.

Reformulation of Acrylic Latexes for use in Flexible Food Packaging.

Your notes:

<u>Bárbara Rezende Lara</u>, T.F.L McKenna, C2P2 – UMR 5265, CNRS/UCB-Lyon 1/ESCPE-Lyon K. Ouzineb, Toray Films Europe

Due their versatility, polymers are widely used in the packaging field. They can be molded in innumerous ways, their properties can be controlled by inserting different compounds or by changing process parameters, their price are very attractive, and, quite importantly, they can be much more easily recycled than glasses and metals. Nevertheless, compared with glasses or metals, polymeric materials are more likely to allow the exchange of low molecular weight compounds, such as gases and vapors. Thus if they are to be used in food packing applications, it is imperative to combine them with other materials in order to prevent the migration of small molecules from the food to the outside and vice versa (1). Using certain metal oxides such as, aluminum oxide, silicon oxide considerably improves the impermeability of polymers to gases, humidity, and other small molecules, as well as allowing one to retain the transparency, which is very important to food packaging application (2). Good barrier levels at thickness in the nanometer range can be provided by aluminum oxide coatings, compared to several micrometers for a polymer-based barrier layers. (3)

The present work aims to improve the adhesion between poly(ethylene terephthalate) (PET) and vacuum deposited metallic aluminum under conditions of high temperature and humidity, by modifying the formulation of an acrylic industrial latex. The main goal is to determine which parameters control the adhesion between the aluminum and the polymer. The addition of reactive functional surfactants, silanes, cure agents, as well as the monomeric composition variation will be analyzed in order to understand which functional group provides the best adhesion force. In addition, polymer properties such as the molecular mass, glass transition, gel content will be studied comparing their influence in the adhesion.

REFERENCES

- 1) SIRACUSA, V. International Journal of Polymer Science 2012, 1
- 2) LOHWASSER, W., FREI, O., SEVERUS, H., & WISARD, A. *Proceedings of the annual technical conference-society of vacuum coaters* 1995, **38**, 40.
- 3) STRULLER, C. F. , KELLY, P. J., COPELAND, N. J. (2014) Surface & Coatings Technology. 2014, 214, 130.

Simulation of Polyurethane/Acrylic Hybrid Polymerization in Batch Miniemulsion Droplets

Your notes:

<u>Shaghayegh Hamzehlou</u>^a, N. Ballard^a, P. Carretero^a, M. Paulis^a, J. M. Asua^a, Y. Reyes^{a,b}, J. R. Leiza^a*

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Waterborne Polyurethane/Acrylic (PU/Ac) hybrid polymers are being studied with the aim of achieving a superior balance of the properties when compared to physical blends and acrylic copolymers. Waterborne PU/Ac hybrid nanoparticles have been used recently to produce pressure-sensitive adhesives (PSAs) with improved adhesive shear strength at higher temperatures, as compared with acrylic PSAs, because the polar groups of the polyurethane may form hydrogen bonds with each other giving rise to a film with better cohesive adhesion. The kinetics and the final microstructure involved in such a system is too complex and hard to study experimentally, so, a detailed kinetic Monte Carlo simulation was used to understand the characteristics of the batch miniemulsion polymerization of an isocyanate and an acrylic monomer mixture that contains a hydroxyl functional monomer (HEMA). The simulation takes into account the simultaneous polyaddition of the polyurethane prepolymer with the hydroxyl group of HEMA and the free radical polymerization of the acrylic monomers, and all reactions in aqueous and polymer particle phases. The model has been assessed by batch miniemulsion polymerizations carried out using an aliphatic isocyanate prepolymer, n-butyl acrylate, 2hydroxyethyl methacrylate monomers and potassium persulfate as an initiator. It was found that partitioning of water had a significant effect on both kinetics and microstructure of the resulting polymer. Evolution of different species of PU prepolymer produced during the reaction and the sol and gel fractions revealed that the terminal pendent double bond of the HEMA in polymer chains have significantly lower reactivity than that of the HEMA free monomer. Detailed information on gel microstructure has been derived in the model by both distribution of molecular weight between crosslinking points in acrylic chains and distribution of chain extension of PU prepolymers. These crosslinking density distributions may be related to mechanical and adhesive properties of the polymer.

Acknowledgments:

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<u>Joseba Juaristi</u>, 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 Tg 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 Tg. 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 (ºC)	>90	>90	85	58	21	13

Table 1: Values of mínimum 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-Tg polymer into a high-Tg crosslinked core can substantially improve the film forming properties of the coatings. However, penetration of the low Tg 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
- 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
- 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

Waterborne Fluoropolymer Dispersions for Hydrophobic Coatings

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Fluoropolymers are useful for a wide variety of applications that range from houseware and medical articles to industrial coatings. All these applications arise from the unique properties offered by these materials, such as chemical inertness, dielectric stability, low friction coefficient, thermal and flame resistance and low surface energy that lead to really interesting applications such as non-wetting properties or self-cleaning materials. Fluoropolymer coatings offer excellent non-stick properties as well as enhanced corrosion resistance¹. Waterborne fluoropolymer coatings would be particularly valuable because they are environmentally friendly.

To prepare waterborne dispersions of these fluorinated materials is necessary to consider the hydrophobic nature of the fluorinated monomers. These monomers are water-insoluble and as they do not diffuse through the aqueous phase, they cannot be polymerized in conventional emulsion polymerization. The incorporation of hydrophobic monomers in the polymer backbone is easier in miniemulsion polymerization. In this process, the monomer is dispersed in an aqueous solution of surfactant using a homogenization device. The particles are formed by polymerizing the monomer droplets. This avoids the need of monomer mass transport through the water².

In addition, it is well known that roughness enhances the hydrophobicity of a solid surface leading to high contact angle values with water³. Accordingly, the combination of hydrophobic materials and roughness constitutes a potential way to obtain these hydrophobic surfaces.

The synthesis of waterborne fluoropolymer dispersions through miniemulsion polymerization and their application for the production of hydrophobic coatings was investigated. Key aspects of miniemulsion polymerization include the control of the droplet size and the stability of the monomer miniemulsion and the development of efficient strategies for droplet nucleation. These aspects were investigated in this work, aiming at synthesizing a broad range of fluoropolymer dispersions with different characteristics. In addition, coatings were cast from these dispersions and from their combination by blending. The effect of the dispersion characteristics on film formation and film properties was studied.

The combination of advanced synthetic methods to fine-tune the characteristics of the polymer dispersions with an appropriate control of the film morphology during the film formation process allowed the production of fluorinated coatings of high hydrophobicity showing contact angle values around 130°.

REFERENCES

- Thomas, R. R; Material Properties of Fluoropolymers and Perfluoroalkyl-based polymers. Springer US, 2002.
- 2) Asua, J. M; Miniemulsion Polymerization. Prog.Polym.Sci, 27, 2002, p. 1283-1346.
- Patankar, N; On the modeling of hydrophobic contact angles on rough surfaces. Langmuir, 19, 2003, p.1249-1253.

Colloidal Stability of PVDF Latex Particles

Your notes:

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Stability of latex particles is a key issue in many emulsion systems, whether it is during the reaction or during post-polymerization treatments. While information on the coagulation of certain well known polymer/surfactant systems is available, to the best of our knowledge there is a lack of information about the coagulation of PVDF latexes stabilised by fluoro-surfactants. For this reason, we investigated the stability of a commercial PVDF latex using turbidity measurements. Typically, the characterization of the colloidal stability are performed using light scattering techniques based on single diffusion model, and the range of operability of this equipment requires dispersion diluted at minimum 1000 times. In this work, we employed a multiple light scattering technique which can be used to study more concentrated dispersions, and so allow us to understand how coagulation takes place in more realistic systems.

Coalescence of the latex particles at different volume fraction was provoked by the addition of an aliquot of a concentrated solution of monovalent electrolyte (NaCl). The backscattering spectra obtain using a Turbiscan Off-line turbidimeter was used to follow the coagulation and to identify the critical coagulation concentration (CCC) of the system under investigation. Additional tests with a polystyrene/SDS system were also performed. The experimental stability data obtained may be used to model the electrostatic stability of the system.

Session III

The Discrete Element Model of Shear-Induced Coagulation – the Structure of the resulting Clusters

Your notes:

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Stabilized colloidal dispersions may be encountered in various products and applications ranging from milk or beer to the production of polymers by emulsion polymerization. The behavior of such dispersions, when subjected to shear, is still not completely understood, especially the processes of shear-induced coagulation and breakage in concentrated dispersions. We used the Discrete Element Method (DEM) for the dynamic simulations of dispersion systems in three spatial dimensions. The interactions between primary particles were described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory for the non-contact interactions and by the Johnson-Kendall-Roberts (JKR) theory for contact mechanics. The morphology of the resulting clusters was characterized by their size (R_a) and fractal dimension (d_f) . For moderately concentrated dispersions (particle volume fraction $\varphi \approx 0.2$), the flow of the surrounding fluid can no longer be assumed independent of the particles. Therefore, we used two-way coupling between the surrounding fluid and the motion of particles. Our results suggest that for a more diluted dispersions (φ < 0.05) the maximum stable cluster size ($R_{\rm g,max}$) is a decreasing power-law function of the applied stress. This corresponds to the breakage-dominated regime. For a more concentrated mixture, the behavior was more complicated due to the increasing importance of coagulation. However, our model was able to capture the dependence of both $R_{g,max}$ and d_f on the system parameters, including the particle volume fraction. Moreover, the morphology of clusters was also the function of time for which the clusters were subjected to shear. A large value of fractal dimension d_{f} indicated dense clusters, which is in agreement with experimental data for shear-induced coagulation from literature. The results of this work provide a theoretical insight into the dynamics of coagulum formation and the structure of the resulting clusters. Apart from the theoretical impact, the results are important for the operation of industrial apparatuses, where they can serve as the constraints of the process conditions in terms of colloidal stability.



(CANCELLED)

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

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"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:

 $R_{c}^{p} = 4\pi . r_{p} . D_{w}[R^{w}] . N_{p} = k_{c}^{p} . [R^{w}] . N_{p}$

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" Fp:

$$k_c^p = 4\pi . r_p . D_w . \overline{F_p}$$

Hansen and Ugelstad [7] also proposed an equation that combines the electrostatic repulsion factor, with capture reversibility to obtain the expression of Fp. 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.

REFERENCES

- Bourgeat-Lami E., N. Sheibat-Othman, A. M. Dos Santos, in Polymer Nanocomposites by Emulsion and Suspension, V. Mittal, Ed., The Royal Society of Chemistry, UK, (2010), p. 269.
- 2) Pickering, S. U. Emulsions. J. Chem. Soc., Trans. 1907, 91, 2001–2021.
- A. Bonnefond, M. Paulis, S. A. F. Bon, J. Leiza, "Surfactant-Free Miniemulsion Polymerization of n-BA/S Stabilized by NaMMT: Films with Improved Water Resistance", *Langmuir* 29 (7), 2397–2405, (2013).
- 4) Smith, W. V., and Ewart, R. H. Kinetics of emulsion polymerization. The Journal of Chemical Physics 16, 6 (1948), 592–599.
- 5) Hansen, F. K. Is there life beyond micelles? In Polymer Latexes, vol. 492 of ACS Symposium Series. American Chemical Society, 1992, pp. 12–27.
- 6) Hansen, F. K. The function of surfactant micelles in latex particle nucleation. Chemical Engineering Science 48, 2 (1993), 437–444.
- Hansen, F. K., and Ugelstad, J. Particle nucleation in emulsion polymerization. A theory for homogeneous nucleation. Journal of Polymer Science: Polymer Chemistry Edition 16, 8 (1978), 1953–1979.

Silica Microcapsules by Templating Pickering Emulsion Droplets: Mechanism of Formation

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On the basis of various analytical techniques, in this presentation a detailed explanation is given about the mechanism of formation of aqueous-core silica microcapsules, produced by templating Pickering emulsion droplets stabilized by silica microparticles. By the consecutive addition of two fluorescently labeled silica precursors and by using confocal fluorescence microscopy, a novel procedure was used to determine that the shell is growing from the inside to the outside. As a consequence, water has to diffuse through the shell to participate in the reaction in the continuous oil phase. It turns out that the initially stabilizing silica particles of the Pickering emulsion are hardly bound to the newly formed shell. It is hypothesized that slow drainage of the interfacial layer around the particles is causing this phenomenon. Knowledge of the growth direction leads to a solid conclusion about the locus of reaction and provides insight into transport of reactants and products through the shell during the silica microcapsule formation. In combination with analytical results obtained from Scanning Electron Microscopy, Light Microscopy, Gas Chromatography, ²⁹Si NMR and Karl Fisher titration, a comprehensive explanation of the mechanism of formation of the silica microcapsules is presented in this contribution.

Figure 1: Fluorescence confocal microscopy images of Rhodamine- Fluorescein-labeled silica microcapsules (top images) and Fluorescein-Rhodamine- labeled silica microcapsules (bottom images). The two dye-labeled triethoxy silicate precursors have been added in aliquots two and four out of five total aliquots of TEOS addition.





Monitoring of Miniemulsion Polymerization of the Methyl Methacrylate in the Presence of Ionic Liquids using Near Infrared Spectroscopy

Your notes:

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In recent years, the miniemulsion polymerization process has been widely studied due to the ease with which it can be used to make hybrid polymer particles with specific morphologies. Compared to other polymerization processes, the process in miniemulsion has some competitive advantages, such as the control of the particle formation, and the encapsulation of compounds into the nanoparticles during the reaction.

In this context, ionic liquids based on imidazolium salts constitute a category of recent stabilizers with a potential for application in polymerization reactors. The performance of these species in the polymerization of miniemulsions is still poorly understood, implying that it is necessary to perform systematic characterization and monitoring studies in order to better evaluate this opportunity. Among the available techniques of process monitoring, near infrared (NIR) spectroscopy has been used successfully for evaluating the properties of polymerization systems. The aim of this work is to develop strategies of online monitoring of methyl methacrylate polymerization reactions in miniemulsion using ionic liquids (ILs) as surfactant. The surfactants used were sodium dodecyl sulphate (SDS), the ionic liquid 1-dodecyl-

3-methylimidazolium chloride and Triton X-405. The studied co-stabilizer was hexadecane (HD), in which its concentration was set at 1, 4 and 7 wt% in the organic phase. The anionic initiator used was potassium persulfhate (KPS) with a concentration of 1 wt% in the aqueous phase and the deionized water was used as continuous reaction medium. The experimental procedure included the mixing of the emulsifiers SDS and Triton X405. After a series of runs the SDS was replaced by the IL. The reactions were conducted in a jacketed reactor and the samples were withdrawn in regular time intervals. Spectra acquisition was carried out in-situ in time-intervals of 5 minutes during reaction. The spectral curves were associated to the reactional medium properties, such as particle average diameter, conversion, number of particles and surface area with the help of linear regression based on partial least squares (PLS) technique generating the calibration model. Such a model was applied for the prediction of the latex properties in real time during the reaction. The results show that the adopted monitoring strategy is excellent for the prediction of the properties. We also observed an improved stability of the particle diameter for those latex containing ionic liquids as surfactant, even when low costabilizer contents were involved. The same thing was not observed when using SDS. Moreover, it was possible to build efficient calibration models for the different properties. In this context, it can be concluded that the NIR spectrophotometer is sensitive to the dynamics of miniemulsion polymerization reactions in presence of IL, thus confirming the promising aspect of the NIR technology for monitoring the properties of the latex.



Stabilization of Emulsions by Using Ionic Monomers

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Emulsifiers play many different roles in emulsion polymerization, such as: nucleation of the latex particles, emulsification of monomer droplets and/or preformed polymer and stabilization of the polymer particles during the polymerization. However, since emulsifiers are not chemically bonded to polymer particles, they bring some undesired effects on the properties of the films prepared from emulsion polymers. These effects depend on many factors such as the chemical nature of the emulsifier and the polymer matrix, the molecular weight and diffusibility of the emulsifier and film casting conditions ^[1].

Emulsifiers may migrate either to film surface and change the gloss properties of the film or to film-substrate interface and reduce the adhesion between the film and the substrate. In addition, if the chemical structures of the emulsifier and the polymer matrix are compatible, the emulsifier may dissolve throughout the matrix and make a plasticizing effect that deteriorates the mechanical properties of the film. On the contrary, if they are not compatible, emulsifier molecules may aggregate as hydrophilic pockets and this in turn increases the water sensitivity ^[2]. Because of these drawbacks, the emulsifier-free emulsion polymerization strategy is followed in this work.

The objective of the study is to develop a synthesis method for emulsifier-free emulsion polymerization of methyl methacrylate (MMA) and butyl acrylate (BA) at low pH values (1.5-4) by using sulfonated functional monomers, specifically sodium styrene sulfonate (NaSS). High solids contents, stable latexes are the specific challenges. By providing covalent attachment of sulfonated functional monomers within the polymer chains, on one hand stabilization of the particles in dispersion will be achieved and on the other, negative effects of emulsifier migration on the resultant film properties will be prevented.

For that aim, MMA/BA/NaSS were polymerized in emulsion by following strategies: a) semicontinous reactions with water as initial charge and b) seeded semicontinous reactions. The effect of different type of initiators (producing water soluble charged radicals or hydrophobic uncharged radicals) on the progress of the reaction was investigated. High solids contents (50 wt%), emulsifier-free stable latexes with 260-335 nm particle size were obtained. The stability of the latexes, particle size, polymerization rate and conversion was dependent on: i) the amount of ionic monomer in the formulation, ii) synthesis method, and iii) initiation region. The hydrophilicity of the polymer films was studied by water uptake and water contact angle measurements and compared with the films cast from latexes prepared by using conventional emulsifiers. The thermal and mechanical properties of the films were also studied.

REFERENCES

- Aramendia E, Mallegol J, Jeynes C, Barandiaran MJ, Keddie JL, Asua JM. Langmuir, 2003, 19, 3212-3221.
- [2] Keddie JL, Routh AF. Fundamentals of Latex Film Formation: Processes and Properties, Ch. 6, Springer, Bristol, 2010.

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Reduced Graphene Oxide/Polymer Composites Latexes by Emulsion and Miniemulsion Polymerization

Your notes:

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Graphene is a novel material with the possibility of being used in many electronic applications in the near future. Water- borne polymers are versatile products used in a wide range of fields; the introduction of graphene into this type of materials could yield immense possibilities of interesting materials with tailored properties.

In here, water-borne reduced graphene oxide (rGO)/polymer composites have been synthesized by mixing and in situ polymerization in emulsion and miniemulsion polymerization systems, starting from stable aqueous dispersions of rGO stabilized by polyvinyl pirrolidone (PVP). With the aim of obtaining stable hybrid latexes capable of forming composites films by water evaporation at standards atmospheric conditions, a polymer system of poly(methyl metacrylate/butyl acrylate) was selected in a proportion of 50/50 wt% in order to achieve a glass transition temperature lower than room temperature.

Differences in structure and conductivity arise from the method chosen to prepare composites, those obtained by blends show weak interactions among rGO platelets and polymeric particles while samples obtained by polymerization in presence of the rGO yield grafting of the polymeric particles to the platelets, resulting in very stable latexes. The formation of the covalent bonds between the filler and particle result in a hindrance to the possible final applications of the composites as conductive coatings as establishing formal bonds with rGO destroys the sp² hybridization of the structure, severally decreasing the electrical conductivity of the filler. Furthermore this reactivity with free radicals makes rGO act as a radical scavenger, decreasing the polymerization rate as the content of it is increased, generating low conversions in the final hybrid latex.

The effect on conversion was mitigated by the use of miniemulsion polymerization and oil soluble initiators, eliminating the propagation step in conventional emulsions reducing the availability of radicals to react with the rGO platelets confined into the aqueous phase.

Nanostructured Polymeric Aqueous Dispersions Containing Quantum Dots

Your notes:

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Quantum dots are semiconductor nanocrystals ranging in size from 1 nm to 10 nm formed from periodic elements of groups II-VI, III-V and IV-VI (CdSe, InAs, PbSe). These nanoparticles exhibit interesting size-tunable electronic and optical properties, like brighter and longer fluorescence time than organic dyes, that allow them to be used in a wide range of applications such as in biology, for photovoltaic devices and light emitting devices^[1,2]. In order to prevent the loose of luminescence because of possible defects in the core surface, the nanocrystal is usually passivated with a semiconductor material, such as ZnS, leading to core-shell structures that are modified with an organic compound (TOPO, ODA...) or an amphiphilic polymer that provide them compatibility in different medias.

Because of their heavy-metal core structure many of these applications require a combination of the quantum dots with polymers creating organic-inorganic hybrid particles^[2]. This polymer covering has two objectives, on the one hand the protection of the environment from the quantum dots toxicity, and on the other hand quantum dots will be protected from photo degradation or damage caused upon mechanical manipulation.

The aim of this project is to encapsulate different types of quantum dots in polymer particles so they can be used as biosensors for multiplexing^[2,3]. Initially for this purpose 7 nm CdSe/ZnS quantum dots coated with octadecylamine as surface modifier have been used in batch^[3,4] and semi-batch miniemulsion polymerization in different conditions. The obtained hybrid organic-inorganic latexes have been characterized using transmission electron microscopy and fluorescence microscopy, using an Olympus BX51 confocal microscope, coupled to a Horiba Fluoromax4 fluorimeter. Different aspects of the experimental work and results will be discussed in the presentation.

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References

- 1) Alivisatos, A.P, Science 271, 933-937, 1996.
- 2) Tomczak, N et al, *Progress in Polymer Science* **34**, 393-430, 2009.
- 3) Joumaa, N et al , Langmuir 22, 1810-1816, 2006.
- 4) Esteves, A.C et al, J. Nanosci. Nanotechinology 5, 766-771, 2005.



SERS Active Substrates based on Ag/Graphene/Polymer obtained by Laser Ablation using Rh6G as a Model Compound

Your notes:

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Designing novel and selective surface-enhanced Raman scattering (SERS) substrates is of interest in sensing applications. SERS technique is a modern analytical tool for chemical and biological detection as well as monitoring of the environmental contaminants, since it allows detection of ultra low amounts of analytes. It provides dramatically enhanced Raman signal from analytes adsorbed onto metal surfaces (usually Au or Ag), due to its significantly broader cross-sectional area of Raman scattering. The observed increase of the Raman signal intensity has been regularly observed on the order of 10⁴-10⁶, and can be as high as 10¹⁴ for optimized systems, reaching up to single molecule detection. Theoretical explanations for the enhancement of the scattered signal are based on two mechanisms: strong electromagnetic field enhancement - so called Electromagnetic Mechanism (EM) and chemical enhancement as a result of formation of a charge transfer complex between the substrate and the analyte - or Chemical Mechanism (CM). These mechanisms have been widely investigated experimentally and theoretically. Graphene gives a clear CM Raman enhancing effect, due to unique 2D structure among other unique properties (efficient quenching of fluorescence in both, the adsorbed analyte and the substrate), which positively influences the quality of Raman spectra. In order to further augment the enhancement of the signal, graphene has been combined with Ag and Au, which results in coupling of EM and CM effects and a significant enhancement of the Raman signal from the adsorbed analytes. Combining graphene with polymers results in quite versatile materials, since polymer introduce excellent bulk physical and chemical properties.

My topic includes preparation of SERS active substrates based on poly(butylacrylate-co-methyl methacrylate) nanocomposites reinforced with up to 3 wt % grahene. Nanocomposite samples were irradiated by a pulsed transversely excited atmosphere (TEA) CO2 laser (Plovdiv University) on the P(20) line of the 0001 \rightarrow 1000 transition (944.19 cm -1) using incident fluence up to 7,3 J/cm² repetition frequency of 1 Hz. Ablation was performed in an evacuated (10⁻³ Pa) pyrex spherical vessel (11 in volume). Thin deposited films with very well distribution of graphene within the polymer matrix were obtained using up to 1500 pulses. The active SERS substates were prepared by subsequent deposition of elemental silver using ArF excimer laser Estonia,Semento) operating at 193 nm, with a repetition frequency of 10 Hz pulse full width at half maximum 23 ns and pulse energy 50 mJ. The ablation time for elemental Ag was 4.5 min, under higher pressure of inert gas Helium. Rhodamine 6G with a concentration ranging from 10⁻⁴ to 10⁻⁷ mol/l was used for measuring the SERS substrate performance. The probe molecule was detected at low concentration and highly enhanced Raman signal was achieved.



Dual Stimuli-Responsive Nanogels: Promising Nanocarriers for Controlled Drug Delivery

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In the past decades, advanced nanoscale carriers for drug delivery have garnered increasing interest in biomedical applications. As vehicles, ideal nanoparticles are obliged to possess stability during circulation in blood, surface functionalities for subsequent bioconjugation/biovectorization, nanometric sizes, biocompatibility and/or biodegradability, high drug loading levels, and ability to deliver drug to the specific pathological site and/or target cells without drug leakage on the way, while rapidly unload drug at the site of actions. To this end, various polymeric particles that release drugs in response to an internal or external stimulus have been actively pursued. In this sense, special attention is paid to environmentally sensitive cross-linked colloidal particles, known as nanogels, as a result of their rather fast capability to change the size (swelling or shrinking) in response to external stimuli such as temperature, magnetic field, biomolecules or pH, among others. This interest also arises from their porous structure that gives them the ability to contain small molecules inside and release them by changing the volume. On top of that, due to their small size, they are able to overcome various biological barriers and achieve passive and active targeting, reducing adverse reactions in tumor therapy. Undoubtedly, taking into account that unhealthy cells and tissues are characterized for having different pHs and temperatures compared to those of healthy ones, nanogels sensitive to these two stimuli are of the greatest significance in biomedical applications, since they could release drugs in the targeted site.¹ In an effort to further fine-tune drug release and augment therapeutic drug efficacy, multi-stimuli responsive vehicles that respond to a combination of two or more stimuli are considered to be highly advantageous, considering their unprecedented control over drug delivery and release.²

Therefore, with biocompatibility³ and stimuli responsiveness to both pH and temperature, a nanogel based on poly(2-diethylamino)ethyl) methacrylate (PDEAEMA) results to have tremendous potential for targeted cancer therapy. In this work, the synthesis of dual-stimuli responsive PDEAEMA-based nanogels was carried out by surfactant-free emulsion polymerization in a batch reactor, using the biocompatible cross-linker ethylene glycol dimethacrylate (EGDMA). In addition, an in-depth study of their tunable swelling behavior was reported, presenting dual-dependent thermo- and pH-sensitivities.⁴ Interestingly, both sensitivities were given at physiologically relevant conditions. Furthermore, a huge variation of the volume phase transition temperature (VPTT), which is the temperature where the phase transition is given, was observed in a small pH range: from 6 to 8, the VPTT varied from 75 °C to 15 °C, making the nanogel more tunable and thus more interesting for bio-applications. Moreover, in order to obtain a deeper insight on their dual-stimuli-responsive behavior, the effect of the ionic strength on both sensitivities was studied thoroughly, considering that it is an important parameter to take into consideration in bio-applications.

Focusing on the synthesis strategy and colloidal characterization for this type of nanogel particles, the latest results obtained in our group will be presented

REFERENCES

- 1) Ramos J., Forcada J., Hidalgo-Alvarez R., Chem. Rev. 114:367-428, 2014.
- 2) Cheng R., Meng F., Deng C., Klok H., Zhong Z., *Biomaterials* 34:3647-3657, 2014.
- 3) Dai S., Ravi P., Tam K.C., Mao B.W., Gan L.H., Langmuir 19:5175-5177, 2003.
- 4) Pikabea A., Ramos J., Forcada J., Part. Part. Syst. Charact. 31:101-109, 2014.

Heat Transfer Phenomena in Micro- and Nano-Cellular Polymeric Foams

Your notes:

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The topic of this contribution is to map all important heat transfer phenomena in micro- and nano-cellular foams and to create a mathematical model, which will help to improve their heat insulating properties. The current generation of heat insulators, which is based on macro-cellular foams, is far from having the optimal properties. Few materials with much lower thermal conductivity were prepared at laboratory conditions. However, both the proper parametric studies and the complete theoretical knowledge on the heat transfer mechanisms is still lacking. As a step to filling this gap, we are using a mathematical model of coupled heat transfer by conduction and radiation to find the theoretical limits of insulation properties for various types of polymeric foams. The developed mathematical model can be used not only for the estimation of foam conductivity of existing materials, but also for the systematic design of new materials with improved properties [1].

We show that a good heat insulator must provide sufficient resistance to both conduction and radiation. Heat conduction can be reduced by increasing the content of low-conducting substance, i.e., by increasing the foam porosity or by the choice of the blowing agent. Moreover, when the cell size is lowered to the order of the mean free path of gas molecules, the mechanism of the heat transfer changes from diffusive to Knudsen mode, and the gas conductivity is reduced to a fraction of its bulk value. Heat radiation is suppressed by the absorption in gas and polymer and by the reflection on phase interfaces. Since the absorption coefficient of polymers is much larger than that of gases, the absorption is more effective when the foam porosity is lower. To estimate the reflection on polymeric wall, the wave interference must be considered, because the wavelength of thermal radiation is usually much higher than the wall thickness and because absorption coefficient of polymers is relatively low. Thus, the fraction of reflected photons depends on the wall thickness, and the optimal number (or number-density) of polymer walls and their thickness must be found in order to minimize the radiative heat flux.

The results of our model show that the low conductivity of the polymeric nanofoam is not guaranteed for all polymers but depends on the type of the polymer as well as on the foam morphology. Moreover, further improvements can be accomplished by creating layered insulators.

REFERENCES

 P. Ferkl, R. Pokorný, and J. Kosek, "Multiphase approach to coupled conduction-radiation heat transfer in reconstructed polymeric foams," *Int. J. Therm. Sci.*, vol. 83, pp. 68–79, Sep. 2014.



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 nonisothermal 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.



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.

REFERENCES

- 1) Samson, Weickert et al.: AlChe journal 44 (1998), p. 1424-1437
- 2) Korber et al.: Macromol. Chem. Phys. 202 (2001), p. 3329-3333
- 3) Pater et al.: Chem. Eng. Sci. 57 (2002), p. 3461-3477
- 4) Al-hay Ali, Weickert et al.: Macromol. React. Eng. 1 (2007), p. 353-363
- 5) Patzlaff, PhD thesis, TU Berlin, 2006

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 $50 - 80^{\circ}$ 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, 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.



Experimental Setups for Heterophasic Propylene Copolymers.

Your notes:

Miguel Plata, Martin Luther University, Germany

Heterophasic propylene copolymers (Hecos's) are versatile polymeric materials used in various applications, for instance in the automotive industry. Heterophasic propylene copolymers consist of a polymer matrix of isotactic polypropylene homopolymer and a dispersed rubbery ethylene-propylene copolymer not miscible with the matrix phase. While the matrix gives good stiffness, the elastomeric phase improves impact strength and low temperature behavior.

Heterophasic propylene copolymers are produced by coordinative polymerization in at least two-stage processes. For heco-PP, commercially predominantly Ziegler-Natta catalysts are used. While the matrix material is either produced in gas-phase or bulk polymerization, the elastomeric phase is produced in all commercial processes by gas-phase polymerization.

For product development, rubber content, rubber distribution and molecular structure of both matrix material and elastomeric material have to be precisely controlled. In coordinative polymerization, the polymerization kinetics depends strongly on the used catalyst system and the polymerization conditions applied. Since there is a continuous development of both new catalysts systems and polymer products, there is a constant need for experimental kinetic data of new polymerization catalysts and for producing polymer samples for establishing of structure-property relationships.

In the contribution, two reactor setups for heterophasic polypropylene polymerization will be presented. One setup for gas-phase polymerization of both matrix and heco-material already exists and has been broadly used already, another setup for bulk-polymerization of the matrix material and subsequent gas-phase polymerization of the elastomeric material is currently build up. Both setups consist of five-liter-reactors, enabling to produce up to 700 g of material per run, which is enough in order to perform mechanical material tests. While the bulk polymerization is done in batch mode, the gas-phase polymerizations are carried out in semi-batch mode and both monomer consumption and gas composition can be monitored. The gained data can be used for development of kinetic models for further product- and process development.



Fouling in a Batch Reactor During an Emulsion Polymerization

Your notes:

Mania Madani, H.- U. Moritz, W. Pauer

Fouling is the general name for the pollution and coating on the walls of chemical reactors. The goal of the work is to extend the understanding and to quantify the influencing parameters for fouling formation during an emulsion polymerization.

Regarding the surface properties it is known that free surface energy and roughness are main parameters responsible for fouling formation. Additionally to these, the testing surfaces were analyzed in more details to gain information about the correlation between the surface properties and the degree of fouling. In that context, the free surface energy, the hysteresis and the wettability by emulsions were determined.

In order to quantify the influencing parameters for fouling formation the amount of fouling was gravimetrically determined on different surfaces. For that purpose, the testing surfaces were fixated within the batch reactor before the emulsion polymerization was started.

The free surface energy was determined by the method of sessile drop. With this method the contact angle between a liquid and the testing surface is measured. The contact angle is defined by the shape of the drop on the three phase contact line between solid, liquid and vapor. This measurement was done with two different liquids on each testing surface. The free surface energy was calculated by the Young-Laplace equation.

The hysteresis of the testing surfaces was determined by using the advancing- receding method. To a drop on a surface a defined amount of liquid is added or removed, while the contact line is pinned. By adding the liquid the contact angle increases (advancing) and by removing the liquid the contact angle recedes (receding). The hysteresis of the regarded surface is the difference between these two measured contact angles.

In order to determine the wettability of the testing surface an emulsion was dosed onto the surface and the contact angle was measured. The smaller the measured contact angle is the better is the wettability of the testing surface. Contact angles larger than 90° correspond to a bad wettability.

Comparing the amount of fouling on the surfaces with the surface properties it was observed that the surfaces with higher surface energy lead to more fouling. Also, the wettability showed an influence on the fouling behavior: the better the wettability the more fouling is formed. The hysteresis provides information about the degree of the roughness of the surface.

Swelling Capability of Hydrophilically Modified Polyurethane Polymers

Your notes:

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Polyurethanes are known for their superior mechanical properties and high resistance against solvents. Nowadays there is an increasing use of aqueous polyurethane dispersions (PUD). These dispersions offer the advantage of a low content of volatile organic compounds. However there is a serious drawback of PUDs. The production cost of these PUDs is much more expensive in comparison to aqueous acrylic dispersions. Therefore it is of interest to develop a system which combines the excellence of PUDs while retaining the low production costs of the acrylic dispersions. These aqueous polyurethane acrylic hybrid dispersions can be synthesized by different routes. One possibility is the preparation of blends of PUDs and acrylic dispersion. A severe disadvantage of these dispersion blends are the poor mechanical properties. Another possibility is the preparation polymerization which offers better results, but exhibits scale up problems. An alternative to these synthesis routes is the possibility to polymerize acrylate in presence of PUDs. These PUDs are prepared from hydrophilically modified Polyurethane polymers (PU polymers). The PU polymers are polymerised using a hydrophilic monomer, long chain diols and isocyantes.

An important property of the modified PU polymer is the swelling ability. Hydrophobic monomers can swell the hydrophilically modified PU polymers and are stabilized by the PU polymer. Higher degrees of swelling allows for more incorporated acrylic monomers after polymerization.

Therefore the swelling behavior of different acrylates in PU polymers has been analyzed. The extent of swelling was determined by analyzing the remaining monomers with gas chromatography. The particle size of the monomer swollen PU polymers and the polymerized polyurethane acrylic hybrid dispersion has been measured by dynamic light scattering (DLS).



Process Intensification through Smart Scale Technology in Continuous Emulsion Polymerization

Your notes:

Kristina Rossow, F. G. Lueth, W. Pauer, H.-U. Moritz, University of Hamburg, Germany

The high specific surface area of a milli-sized tube reactor (length: 10 m, inner diameter: 10 mm, production volume in range of kg/h) provides certain benefits in matters of heat-transfer, inherent process safety and therefor offers a high potential in process intensification.¹ By means of a case study the characteristics of an emulsion copolymerization in a milli-sized tube reactor are presented in terms of e.g. conversion slopes, molecular weight distribution and particle sizes. The impact of process parameter variation such as the molar ratio of the monomers, the monomer/water ratio and different operation modes are shown. Besides the poster shows the experimental set-up and gives an overview of the reactor properties.

Using PTFE as reactor material offers a lot of advantages referring to surface fouling¹ and flexibility in reactor design. The helical coiled reactor geometry, leading to secondary flow phenomena² like dean vortices, in combination with integrated static mixing elements³ results in narrowed residence time distribution and improved heat transfer properties.¹ The combination of reactor geometry and material enables the stable realization of copolymerization reactions in a wide range of solid content throughput of up to 40 per cent per weight without any form of polymer deposit on the reactor wall and therefor without changes in the reactor properties. Besides the used reactor set-up and the case study emulsion show a good stability towards temperature disturbances in the inlet as well as in the jacket temperature of more than 15 °C. This robustness of the system towards external disturbances allows a wide application range by means of online feedback control.

In order to get information about the progress of the reaction the experimental set-up is designed to allow sampling at various residence times without influencing the mass flow, thus the flow properties and the final product. That way a lot of reaction properties as the total conversion, the particle size, temperature can be gained by a single experiment for different reaction states.

REFERENCES

- 1) F. G. Lueth, W. Pauer, H.-U. Moritz, Properties of Smart-Scaled PTFE-Tubular Reactors for Continuous Emulsion Polymerization Reactions, *Macromol. Symp.*, **2013**, *333*, 69–79.
- W. Pauer, H.-U. Moritz, Continuous Reactor Concepts with Superimposed Secondary Flow – Polymerization Process Intensification, *Macromol. Symp.*, 2006, 243, 299–308.
- J. Schmidt, Kinetische Und Reaktionstechnische Untersuchungen Zur Kontinuierlichen Schnellen Emulsionspolymerisation, Hrsg. H.-U. Moritz, Wissenschaft & Technik Verlag, Berlin, 2010.

Continuous Emulsion Copolymerization of Vinyl Acetate in a Laminar Stirred Tube Reactor (LSTR)

Your notes:

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Commonly polymer dispersions are produced in batch or continuous tanks in series. The main drawback of these processes is the poor space-time yield. Furthermore large plants with big reactor inventory and small surface to volume area are used. Thus the reactor performance of these processes is limited. There are some attempts ^[1,2] for continuous polymerization of vinyl acetate in reactors with pipe like residence time distributions. These processes have main drawbacks due to scale up and durability compared to the concept of this presentation.

In this work a laminar stirred tube reactor for continuous emulsion copolymerization of vinyl acetate and VeoVa 10[™] is studied. This reactor combines the concept of the tube reactor with the continuous tanks in series congenially and offers a large surface to volume area. Furthermore heat transfer or the residence time distribution can be tuned by parameters like aspect ratio of the reactor, geometry and velocity of stirring shaft.

In this presentation the continuous polymerization plant will be presented. The dependence of conversion, particle sizes due to process parameters like throughput, stirrer velocity and geometry are shown. Furthermore the temperature and conversion profiles along the reactor axis are discussed regarding to the residence time distributions characteristics of the laminar stirred tube reactor.

Finally in this presentation the feasibility of the laminar stirred tube reactor for producing high solids content latexes is shown.

REFERENCES

- 1) T. Melchin, *Kontinuierliche Emulsionspolymerisation grobteiliger Latices*, University of Hamburg, **2011.**
- 2) M. Babar, Continuous Emulsion Copolymerization of Vinyl Acetate and VeoVa 10 using Taylor Reactor, University of Hamburg, **2012**.

Cloud Point Pressure Curves of High Density Ethylene-Acrylate Copolymers

Your notes:

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During the high pressure polymerization process of polyethylene and polyethylene copolymers it must be ensured that polymerization takes place in homogeneous single phase, to obtain a uniform product of high quality. Therefore, a good knowledge of phase behavior of the reaction mixture is crucial. Measuring of cloud-point curves provides a facile method to determine the boundary between single and two-phase area.

Copolymerization represents an effective way to modify polymer properties. Even small incorporation ratio of comonomer cause great changes. Copolymerization of ethylene with polar comonomers occurs present by free-radical polymerization. The resulting copolymer consists of short- and long-chain branches. Catalytic polymerization offers a way to achieve linear microstructured polyethylene. However copolymers with polar comonomers, by using common industrially catalyst, like Ziegler-Natta and Metallocens, cannot be achieved. Such catalyst based on early transition metals which show high oxophilicity. Thereof results strong bonds between metal and polar group.

Novel late transition metal catalyst with general formula (NiPh(P,O)) are less oxophilic, which allows the copolymerization of ethylene with polar comonomers. In our working group we investigate the influence of high pressure and temperature (up to 2000 bar and 200°C) on the copolymerization behavior of such catalysts which are also known as SHOP-type-catalysts (Shell Higher Olefin Process).

In this work cloud-point curves of high-density ethylene-methyl acrylate and ethylene-n-butyl acrylate copolymers in supercritical ethylene and accordingly comonomer as solvent have been measured. The measurements are carried out in an optical high pressure view cell with moving piston up to 2000 bar and 260°C. The influence of different comonomer incorporation ratio on the cloud point pressure point was examined.

High-Temperature Emulsion Polymerization of Styrene and N-Butyl Acrylate

Your notes:

Alisa Gapchenko, H.-U. Moritz, W. Pauer, University of Hamburg, Germany

This work focusses on several aspects regarding the emulsion copolymerization of styrene and butyl acrylate at elevated temperatures. Processes with reaction temperatures above 70°C have not been sufficiently investigated yet; the particular interest of this work concentrates on batch reactions in the range of 70°C up to 180°C. An increase of temperature results not only in an increase in the polymerization rate but also in background polymerization processes (such as backbiting, ß-scission, thermally initiated polymerization, etc.). Those processes along with the reaching of the ceiling-temperature can be crucial in the mechanism of polymerization and may eventually replace the use of initiators.

All the styrene butyl acrylate emulsion polymerization experiments were carried out in an automated reaction calorimeter at a starting pressure of 2 bar and nitrogen atmosphere. The solids content was 11 wt% with the styrene/butyl acrylate ratio of 50/50 mol% for each selected reaction temperature. The mechanism of the polymerization was examined through the obtained calorimetric data, the molar mass and particle size distributions, the conversion of monomers and NMR.

Up to 110°C a rate maximum was reached at a similar conversion, implying the simultaneous beginning of the Interval III (disappearance of monomer droplets), however the constant rate period (Interval II) disappeared due to the combination of nucleation and propagation reactions. At higher temperatures the amount of self-initiated processes increases, at 180°C no differences in conversion of thermally and radically initiated reactions was observed. An increase of the polydispersity index as well as particle size was observed for reaction temperatures higher than 110°C. An extended comparison with literature data shows the need of review of the classic emulsion polymerisation mechanism for high temperature processes.



Influence of various Agents on the Radical High Pressure and High Temperature Ethylene Polymerization

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Although low density polyethylene is a very common and widely used polymer it still poses challenges for reaction engineers. This contribution deals with the structural gap between polyethylene formed by catalytic reactions and free radical ones: Polymer manufactured by catalytic processes is linear and long chain branches are introduced by comonomers. In radical polymerization processes of ethylene the molecular architecture is developed depending on process conditions such as temperature and pressure. However, these reaction parameters can only be varied in a range limited by the need of one-phase-systems and the threshold of ethylene decomposition.

Polymers with a lot of long chain branches, less short chain branches and low PDI cannot be formed by either of the mentioned processes. This contribution deals with additional agents, which are able to interfere in the radical polymerization mechanism and could possibly lead to such tailor made polymers. Methods and experimental set-ups to determine the influence of those substances have been tested.

Before testing the agents in polymerization systems they have to be checked with regard to their stability in ethylene up to 2000 bar and 330 °C. A high pressure differential thermal analysis (HP-DTA) setup is used for this examination. In addition, the phase behavior of the substances is analyzed in a high pressure viewing cell. To ensure an invariable composition during the experiment containing temperature and pressure scans the inner volume of the cell is adjusted by a moveable seal.

The final polymerization experiments are conducted in a stirred high pressure batch reactor with injection system for initiator and additional substances. All experiments have an initial pressure of 2000 bar whereas the start temperature is modified between 160-170°C and the duration of an experiment varies between 1 minute and 24 hours.

Two classes of initiators (e.g. Figure 1) with different decomposition kinetics are used. TBPEH is a peroxide with its half life time in the range of seconds at reaction conditions. Representing a more stable hydroperoxide, TOHP possesses a half life time of up to several hours. In order to enhance these characteristics even more, TBPEH is added to the reaction mixture at high temperatures while TOHP is adjoined at low temperatures with subsequent heating.

The structural properties of the received polymers and the state of the added agents are analyzed by (LS-) GPC, IR and high temperature NMR.



TBPEH TOHP Figure 1: Mid-temperature initiator TBPEH (Tertbutyl-per-2-ethyl hexanoate) and hightemperature initiator TOHP (1,1,3,3-Tetramethylbutyl hydroperoxide) used in different sessions to test the agents influence on the radical polymerization