1999

17th International Herman F. Mark Symposium: Polypropylene - a Material of the Future

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Helga Roder and Otto Vogl, *17th International Herman F. Mark Symposium: Polypropylene - a Material of the Future,* Polymer News, 24(7), 241-245 (1999); Progress in Polymer Science, 24,1205-1216 (1999)

Conference Report

17th International Herman F. Mark Symposium: Polypropylene – a Material of the Future

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Two scientists, inventors and industrial leaders were elected this year to receive the prestigious Herman F. Mark Medal of the Austrian Research Institute of Chemistry and Technology for their outstanding contributions to the scientific and technological developments of polypropylene. The medals were presented to Professor Paolo Galli, President of the Technology Company of Montell and to Professor Manfred Rätzsch, Research Director of PCD-Polymere, a subsidiary company of OMV, the Austrian oil company. PCD-Polymere has, since the announcement of the Herman F. Mark Medals, become a part of the Borealis A.G. located in Denmark. The presentation of the Mark medals was highlighted with a Symposium on polypropylene, a subject closely related to the achievements of the recipients.

The 17th International Herman F. Mark Symposium with the title **Polypropylene – a Material of the Future** was held on November 11 and 12, 1998 in the ***Beletage*** of the Austrian Trade Association in Vienna, Austria. About 150 participants who came from 8 countries, attended the Symposium. The Conference was organized by the Austrian Research Institute of Chemistry and Technology and was held under the auspices of the Ministry of Science and Transportation

The Symposium was opened by Dr. Hans J. Kaluza, the President of the Austrian Research Institute of Chemistry and Technology. He presented a historic view of the importance and the impact that Herman F. Mark had on the scientific development of polymer science and plastics technology in Austria and in the world.

Dr. Paul Salajka, Deputy in the Ministry of Science and Transportation pointed out how important it was for the Ministry (Department) of Science and Transportation in Austria to sponsor and support the presentation of the Mark medals. The Mark medal represents the recognition of outstanding scientists and technologists of high international standing, related with Austria and with the legendary Professor Herman F. Mark, a born Austrian, who was teaching early polymer chemistry and physical chemistry in Vienna in the 30's. Dr. Paul Salajka mentioned that the Federal Minister of Science and Transportation, Caspar Einem, was committed to personally present the Herman F. Mark Medals to the recipients.

The Symposium consisted of 22 Lectures.

The Conference was opened with the opening talk by Professor Otto Vogl, Herman F. Mark Professor of Polymer Science Emeritus of Polytechnic University, now at the University of Massachusetts. Professor Vogl who was closely

Helga Roder

Otto Vogl

associated with Herman F. Mark for much of his life presented the present status and possible future development of polypropylene and his own personal relationship with polypropylene. The speaker pointed out that the Conference should be more properly called **Polypropylene – THE Material of the Future**.

Otto Vogl of the University of Massachusetts, Amherst, MA, U.S.A.: *Polypropylene: An Introduction:*

Since the discovery and invention of polypropylene in 1954 and the beginning of commercial production by Montecatini in Ferrara in 1957, the production and use of polypropylene has made spectacular progess. One of the reasons for polypropylene's commercial success is that major parts of the polypropylene market require properties of "Engineering Plastics" character, at polyolefin prices. In 1997, polypropylene was produced in 157 plant locations in 44 countries. By the year of 2000, about 30 million tons of polypropylene will be produced world-wide which amounts to over 15% of the entire plastics production. Polypropylene is still the fastest growing commodity plastic.

Paolo Galli of the Montell Technology Co. B.V. Hoofddoep, The Netherlands: *The Reactor Granule Technology and the Expansion of the Polypropylene Properties and Technologies:*

Continuous and fascinating developments in the polypropylene field has resulted in outstanding commercial growth. Continuous expansion of its properties has been made possible by the progress in both catalyst performances and process technologies. The first important breakthrough was the discovery of the magnesium chloride support for the active

Polymer News, 1999, Vol. 24, pp. 241 – 245
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Paolo Galli

Luciano Luciani

transition metal catalyst. This brought about an increase in polymer productivity by an order of magnitude. Even more important was the recognition and the industrial use of the "replication phenomena" by the parent catalyst particle to form the final polymer. This technology has become known as the "granule technology".

The heterogeneous catalysis and the understanding of the complex mechanisms has opened new dimensions, to decide the morphology and the internal and external structure of the polymer granule. This technology has allowed the preparation and development of polymers with new properties and applications, the exploration of versatile process technologies and the minimalization of the ecological impact of such polymerization processes.

In the new reactor granule technology it is not only possible to use 4th, 5th and 6th generation Ziegler-Natta type catalysts for olefin polymerization, but also radical, anionic, cationic and metallocene type initiators selected for the appropriate polymerization systems. The crowning of the potentials found to date is the possibility of different and mixed materials in the Multizone Reactor Granule Technology.

Michael-Joachim Brekner of the Tragor Ges.m.b.H., Mainz, Germany: *Metocene-Technology: An Outstanding Tool for Improving and Designing Polypropylene Property Profiles:*

Metallocenes have been recognized as potentially very important advanced catalyst components for the polymerization of olefins. At the beginning of this decade high performance metallocenes having the ability to catalyze the formation of polypropylene of high molecular weight and high isotacticity were discovered.

Tragor is the name of the joint venture between Hoechst and BASF for the scale-up of the polymerization of propylene and the commercialization of polypropylene, based on metallocene catalysis. Unique properties of metallocene based polypropylene are transparency and high modulus, needed for thin wall packaging, and also providing advantages in textile and film applications.

Hubert Puchner of Borealis A.G., Linz, Austria: *Market Trends, Developments and Chances of Polypropylene:*

Polypropylene is continuously taking over new markets because of the competitiveness of its price/performance behavior. While the price is expected to soften somewhat in the near future, new applications and penetration in other markets will guarantee the continuation of the growth pattern.

Kent Abbås of Borealis A/S, Lyngby, Denmark: *The Added Value of Polypropylene:*

Kent Abbås

There is a dynamic development in the polyolefin areas. Not only do we see the structuring and restructuring of the industry, but we also see new generations of materials and breakthroughs in research and development. The chemical structure of polypropylene offers opportunities for the development of highly sophisticated materials. Highly effective Ziegler-Natta type catalysts and single site catalysts provide the production of a wide selection of many versatile materials, based on stereochemistry, molecular regularity and morphology. We see increased emphasis on development of new polymerization processes and their applications, including our new process of supercritical propylene polymerization techniques.

Rolf Mülhaupt of the Albert-Ludwigs-Universität Freiburg, Freiburg i. Br., Germany: *New Polypropylene Materials:*

Since the pioneering work in the 1950's polypropylene has emerged as an environmentally friendly material which combines low cost with high versatility in applications and recycling. Polypropylene competes successfully with other engineering plastics. Modern catalyst and process generations give excellent control on molecular and supermolecular structures. Highly active and stereoselective catalysts provide the strong base for reactor granule technology, gas phase polymerization and reactor blends. Orientation, nucleation, filler addition provide new polypropylene engineering plastics with improved toughness/stiffness balance.

At the Restaurant in the Hotel Sacher

Wolfgang Neissl of Borealis A.G., Linz, Austria: *From Soft to Stiff Polypropylene – a New Generation of Borealis Duplex:*

Low temperature performance of polypropylene is limited because of the relatively high glass transition temperature and a rubbery phase (EPR) has to be added to the semicrystalline polypropylene matrix. Today this can be accomplished using modern catalyst and polymerization technologies in multistage reactor arrangements. In another approach matrix and EPR are

matched in an optimized way leading to flexible, transparent materials for such challenging markets as the automotive industry.

To boost stiffness of polypropylene it is important to understand and have complete control of the crystallization behavior of polypropylenes including the use of polypropylene of high stereoregularity combined with clever nucleation strategy.

Markus Gahleitner of Borealis A.G., Linz Austria: *Rheology as a Quality Control Instrument*:

The speaker discussed in great detail how important it is to know in detail the flow characteristic of polypropylene in order to guarantee the quality and reliability of the production of the final product.

Jean-Roch Pauquet of CIBA Spezialitätenchemie A.G., Basel, Switzerland: *Breakthrough Chemistry for Processing Stabilization of Polyolefins*:

The constant need to improve the technical performance of existing polyolefin grades in a highly competitive environment and the advent of new catalyst technology leading to new applications require ever more effective stabilizer systems.

Several new high performance products have been introduced as alternatives to the traditional binary systems. These high performance products offer superior performance and increased productivity while maintaining the performance of the polymer in demanding applications. These new products are synergistic mixtures of sterically hindered phenol and phosphite processing stabilizers boosted by a small amount of a lactone (3-arylfuran-2-one)stabilizer. The latter is a revolutionary new processing stabilizer for polyolefins which functions by the formation of a highly stabilized benzofuranyl radical by easy donation of the weakly bonded benzylic hydrogen atom.

Reinhold W. Lang of the Montanuniversität Leoben, Leoben, Austria: *Fracture Mechanical Characterization of Polypropylene*:

It was pointed out how important it is not only to characterize polypropylenes from the point of view of chemical structures and basic structure/property relationship and rehological behavior but also by the charcacterization of their fracture mechanical behavior.

Manfred Rätzsch of Borealis A.G., Linz, Austria: *Special Polypropylenes for a Developing and Future Market*:

The importance of polypropylene has developed into a family of thermoplastics based on different molecular structures. As chemical structures they are based on stereoregularity, the degree of stereoregularity and the distribution of stereoregularity. The mechanical properties are also dependent on the relationship of the well known crystalline phases of polypropylene. Possibilities exist in the effective use of catalysts to produce polypropylenes of various regularities, with fillers that optimize desirable polymer properties.

Manfred Rätzsch

The immediate industrial and company objectives are both soft, supersoft and stiff materials. Additional areas of thrust are the development of highly branched polypropylenes for high melt strength for film blowing and grafted polypropylenes based on solid state grafting.

Eberhard Borsig of the Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovak Republic: *Polypropylene Derivatives*.

In spite of the spectacular growth of polypropylene it suffers a major deficiency – poor interaction with other materials. Chemical modification of polypropylene can ease or suppress these deficiencies. Functionalization in the laboratory have led to efficient functionalization and grafting onto polypropylene. It involves chemical modification by photochemical and by high energy radiation initiation. Very few and selected techniques are suitable and have been introduced for industrial applications.

Wolfgang Geymayer of the Center of Electronmicroscopy, Graz, Austria: *Microscopic Investigations of Specialty Polypropylenes*.

The structure of polypropylene and the properties of the different morphologies have been evaluated. Structures that have been obtained under different conditions of injection molding and extrusion, with special emphasis of interphases, were evaluated.

Leopold Katzmayer of Gabiel Chemie Ges.m.b.H., Gumpoldskirchen, Austria: *Additives for Polypropylene*:

Polypropylene has developed into one of the most useful plastics materials. It has inherently most attractive properties among them a relatively low price. It is capable of a wide variety of possibilities for modification. Still polypropylene must be stabilized in various ways, because it is a hydrocarbon polymer, which has some disadvantages. Most additives have polar character which are not compatible with the base polymer. Among the additives that are needed are pigments, carbon black, flame retardents and dyes. A major problem has been the efficient dispersion of carbon black on a commercial scale. The combination of UV-stabilization with halogen containing flame retardents has led to marginal success but has not been efficientiy solved.

Otto Vogl *Dieter Freitag* *Paolo Galli*

Christa Hametner of the Austrian Plastics Institute, Vienna, Austria: *Polypropylene Pipes for Drinking Water Uses*:

Polypropylene pipes have been considered for use in drinking water applications, especially in the area of warm water uses. Polypropylene must be stabilized with antioxidants and fabrication stabilizers. Properly selected higher molecular phenol

antioxidants and phosphites can provide polypropylene pipes that can fulfill the hygienic requirement for materials used in drinking water applications even for warm water uses.

Walter Baumann of Borealis A/S, Lyngby, Denmark: *High Performance Polypropylene's for Exterior Body Panels*:

Polypropylene is becoming more and more the material, the polymer of choice in use for automobile construction because of its adequately high performance at low weight.

Georg H. Michler of the Martin-Luther Universitaät Halle Wittenberg, Halle, Germany: *Micromechanical Mechanisms for Toughness of Polypropylene and Polypropylene Combinations*:

A profound knowledge of the relationship between morphology and deformation properties of polymers is important for the development of polymer systems with improved mechanical properties. Such structure property relationship can be understood by better knowledge of micromechanical processes of deformation and fracture. In heterogeneous blends with improved mechanical properties micromechanisms depend strongly on the phase morphology, structure and properties of interfaces.

Polymer toughness is often the decisive property. Optimal toughness can be achieved by using modifier particles with different physical properties which control the plastic deformation processes in the matrix.

With impact modified polypropylenes, plastic deformation takes place through the mechanism of multiple shear deformation. Polypropylene blends with EPR provide blends which have effects below the glass transition temperature of the rubber phase and provide a new low temperature toughening mechanism. Polypropylene modified with inorganic fillers shows both increased stiffness and toughness.

Manfred Arnold of Martin-Luther Universität Halle-Wittenberg, Halle, Germany: *Modified Polypropylene by Metallocene Catalysis*:

Much of the growth of polypropylene is expected to come from the development of new metallocene catalysts. The synthesis of propylene/1-olefin copolymers lead to products with a multiplicity of new materials properties. Random incorporation of a variety of side chain lengths in the propylene copolymers can lead to polymers with a wide range of properties from thermoplastics to thermoplastic elastomers and to the properties of regular diene polymers. The synthesis of propylene/1-olefin copolymers with high propylene content shows that by random incorporation of only a small amount of 1-olefins, the crystallinity of polypropylene is significantly reduced which leads to a decrease of the melting temperature.

Metallocene catalysts also allow the incorporation of cycloolefins without ring opening which lead to copolymers with interesting properties. Of additional interest is also the preparation of graft polymers. Such polymers are obtained by copolymerization of norbornenyl terminated polystyrene macromonomers or allyl-terminated polyisobutylene macromonomers with propylene via metallocene catalysts. Such polymers can be used as such or as compatibilizers for polypropylene/styrene or polypropylene/polyisobutylene blends.

Hans-Gerhard Fritz of the Universität Stuttgart, Stuttgart, Germany: *Innovative Polypropylene Blends by Reactive Compounding*:

The production of novel polymeric two phase-materials are important for regular producers as well as for users to make composites. Because of facilities and new techniques of processing these areas are fruitful places of activities for companies qualified in fabrications. They provide room for niche projects which would normally not have room on the commodity market, because of their relatively small volume.

Propylene (co)polymers prepared by metallocene catalysts provide materials that could provide properties with highly optimized property profile. It will allow the preparation of heterophase polypropylene blends by using cascade arrangements of the twin screw extruder for the preparation of such blends by new developments in thermoplastic elastomers, thermoplastic vulcanizates based on polypropylene-ethylene/1-octene copolymers, and new properties of innovative two phase materials.

Georg Steinbichler of Engel Maschinenbau Ges.m.b.H., Schwertberg, Austria: *Innovation Potential for New Injection Molding Processes*:

The dominating position that polypropylene has achieved is based on a number of factors, particularly the excellent price/property relationship and the extensive possibilities to modify the mechanical properties as well as the superior fabrication possibilities. Polypropylene is gaining in innovative fabrication techniques and new possibilities in injection molding, particularly in the automotive industry. Polypropylene is taking now a leading position with 100 lbs. of propylene polymers for many cars.

The following new and adjusted techniques should be mentioned: Technique of thin wall injection molding and co-injection molding, surface decoration and low pressure techniques, integration of functions with multicomponent techniques, for structural building blocks reinforcements with long fibers and several additional technology developments.

Hans-Joachim Radusch of Martin-Luther Universitaät Halle Wittenberg, Halle, *Germany: Thermoplastic Elastomers Based on Dynamically Crosslinked Polypropylene-Rubber Blends*:

Dynamic vulcanizates have established themselves successfully as a separate group of materials in the family of thermoplastic elastomers. The advantage is in the flexibility of their adjustments to the appropriate application. This is achieved by the possibility of using the most different thermoplastic – elastomer combinations but as the possible use of varied crosslinking systems with additional modifications.

Most importantly the dynamic vulcanization occurs during the dispersation of the polymer phase with the crosslinkable elastomer phase. Examples are polypropylene and EPDM, polypropylene/natural rubber, polypropylene/butyl rubber and polypropylene/SBR rubber.

Karl Ebner of Borealis A.G., Linz, Austria: *Polypropylene Properties and Applications in the Buildings Industry*:

The use of polyolefins in the building industry plays a only a second role as compared to the packaging. Typical products are in pipes of polypropylene and crosslinked polyethylene. High modulus polypropylene is playing a more and more dominant role. These can be prepared by β-nucleation of polypropylene using special nucleating agents. The excellent property profile of pipes of β-nucleated polypropylene is characterized by better impact resistance at low temperatures, better resistance to fracture which is the basic requirement for pressure pipes and ultimately chemical resistance.

Selected papers of the 17th Herman F. Mark Symposium are scheduled to be published in a special issue of the Journal of Macromolecular Science, Pure and Applied Chemistry, A36, (1999) with Eberhard Boesig and Otto Vogl as the Guest Editors.

Otto Hinterhofer

Manfred Rätzsch Caspar Einem Paolo Galli

Anna Maria Galli

Presentation of the Herman F. Mark Medal: Under the chairmanship of Professor Otto Hinterhofer, the Head of the Austrian Research Institute of Chemistry and Technology, the Herman F. Mark Medals were presented at the ***Beletage*** of the Austrian Trade Association in the late afternoon of Wednesday, November 11, 1998. Federal Minister for Science and Transportation, Caspar Einem, in the presence of the President of the Austrian Research Institute of Chemistry and Technology, Dr. Hans J. Kaluza presented the Awards.

The LAUDATIO for Paolo Galli was presented by Dieter Freitag, Director of Materials Research of Bayer A.G. Present was also Mrs. Anna Maria Galli, several coworkers from Ferrara and Aurelio Pariali, the Mayor of the community of Portomaggiore in Italy.

The LAUDATIO for Manfred Rätzsch was presented by Gerhard Roiss, Executive Vice President of OMV and responsible for Borealis. Mrs. Christina Rätzsch and a number of Rätzsch's coworkers from Borealis Linz also attended the ceremony.

Dieter Freitag Josef Schurz Gretl Schurz

Aurelio Pariali Dieter Freitag Paolo Galli

At the Griechenbeisel

The Award Ceremony was followed by a dinner for the recipients and the invited guests which provided an opportunity the meet old friends and a congenial interaction of all the participants.

The Symposium ***Polypropylene – a Material for the Future*** was scheduled to open in the morning of Wednesday, November 11, 1998. A number of the participants, especially the speakers, arrived on Tuesday. Consequently the organizers, headed by Otto Hinterhofer, had arranged an evening "get-together" with dinner at one of the most famous Restaurants Vienna, the "Griechenbeisel". This Restaurant is the oldest restaurant in Vienna and had been in continuous operation since the 15th century. Parts of the building are even older. This time of the year in Austria, it is traditional to celebrate the anniversary of St. Martin on November 15. This festivity is recognized by a traditional meal of goose, red cabbage and dumplings. The Griechenbeisel restaurant provided exceptional examples of this meal for the dinner of the speakers.

During the Symposium, the buffet style luncheons were provided by the Symposium organizers. These traditional lunch arrangements for the Herman F. Mark Symposia, simplify the luncheon needs and, at the same time, keep the participants from dispersing throughout Vienna in search for the "right" restaurant and also to provide a nice atmosphere of camaraderie.

This most successful Symposium was closed on Thursday afternoon by Dieter Loidl, the Director of the Austrian Plastics Institute. From the lower attendance in the late afternoon, it became evident that the participants from out of town had started to take advantage of the beauty and the excitement that Vienna, Austria and polymer science in this atmosphere can provide.