Plenary lectures

The market and manufacture of polyolefin in China

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The polyolefin consumption grows very fast in China. However, the polyolefin Capacity grows much faster than consumption does not only in China, but also in many other Asian countries. Therefore, the market competition is also intense in China. As a main polyolefin producer, SINOPEC has to develop high performance polyolefin grades with lower cost to avoid the hot competition. Some newly developed polyolefin materials, such as high speed and high stiffness BOPP, low cost HCPP and PE-100+ etc. based on our new polyolefin catalyst, new polymerization process and new additives, will be introduced in this talk.

BIOPLASTICS: STATE OF THE ART, PROPERTIES AND ENVIRONMENTAL IMPACT

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The demand for biodegradable polymers is steadily growing since ten years at an annual rate between 20 and 30%. The market share, however, is still very modest accounting for less than 0,1% of the total plastics market. Today the bioplastics available in the market at different level of development are mainly carbohydrate based materials. Starch can be either physically modified and used alone or in combination with other polymers, or it can be used as a substrate for fermentation for the production of polyhydroxyalkanoates, lactic acid, transformed into poly lactic acid (PLA) through standard polymerisation processes. It is also possible to transform carbohydrates in chemical intermediates such as 1,3 propandiol or succinic acid. Another interesting sector of development relates to chemical intermediates from fatty acids and glycerol. Main present applications of bioplastics are in agriculture, hygiene, packaging, food serviceware, wrappings, waste management, transportation. The increasing use of bioplastics can open to entirely new generations of materials with new performances in comparison with traditional plastics. Moreover the characteristic of bioplastics to recycle CO2 and/or to biodegrade minimizing the risks of pollution can offer significant environmental and social benefits in a wide range of disposal options such as sewage sludge water treatment plants, composting, incineration.This paper will review the state of the art and the potential of different bioplastics. Moreover it will make reference to the Novamont's model of Biorefinery integrated in the Territory. The case is a simple and tangible demonstration of the potential of bioplastics and SMEs in experiencing new economical models based on the qualification of the local area in terms of minimization of the environmental impact and on the integration and partnership with the different stakeholders.

Processing Controlled Polymorphism of Syndiotactic Polystyrene

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The lecture deals with the polymorphic behavior of syndiotactic polystyrene and its control by processing. In the first part, melt processing conditions that allow controlling the formation of α and β crystalline phases, both including zig-zag planar chains, will be described. In particular, procedures suitable to get the thermodynamically stable solvent-resistant β phase will be discussed. Most of the lecture will be devoted to fabrication processes in the presence of suitable solvents, mainly leading to co-crystalline phases between host helical s-PS chains and low molecular-mass guest molecules. Depending on the chemical nature of the guest molecules clathrate1 and intercalate2 co-crystalline phases can be achieved. It will be also shown that suitable processing conditions can lead to the unprecedented formation of films with three different kinds of planar orientations of the co-crystalline phase.3Suitable guest extraction procedures (e.g., by carbon dioxide in supercritical conditions) from polymeric materials including co-crystalline host-guest phases, can produce two nanoporous crystalline phases (δ and ε), which are able to absorb guest molecules also from very dilute solutions. δ4 and ε5 crystalline phases of s-PS present their nanoporosity organized as isolated cavities and channels, and generally absorb guest molecules with their molecular planes roughly perpendicular and parallel with respect to the polymer chain axes, respectively. To our knowledge, δ and ε crystalline phases of s-PS are presently the only known polymeric nanoporous crystalline phases.Aerogels including the two nanoporous phases can also be easily obtained by solvent removal by carbon dioxide in supercritical conditions from s-PS physical gels.6 These aerogels are particularly suitable to increase the guest sorption kinetics.The final part of the lecture will be devoted to possible advanced applications of co-crystalline and nanoporous crystalline s-PS samples. In particular, applications of nanoporous films for molecular sensor,7 for sensors of chirality8 and for active packaging of fruit and vegetable (by removal of ethylene and carbon dioxide) and of co-crystalline films for optical memories9 for fluorescent10 and dielectric11 materials will be presented.

(1)(a) Chatani, Y.; Shimane, Y.; Inagaki, T.; Ijitsu, T.; Yukinari, T.; Shikura, H. Polymer 1993, 34, 1620;.(b) De Rosa, C.; Rizzo, P.; Ruiz de Ballesteros, O.; Petraccone, V.; Guerra, G. Polymer 1999, 40, 2103.(2) a) Petraccone, V.; Tarallo, O.; Venditto, V.; Guerra, G. Macromolecules 2005, 38, 6965. b) Tarallo, O.; Petraccone, V.; Venditto, V.; Guerra, G. Polymer 2006, 47, 2402. (3)a) Rizzo P, Lamberti M, Albunia A R, Ruiz de Ballesteros O, Guerra G. Macromolecules 2002; 35; 5854. b) Rizzo, P. Costabile, A.; Guerra, G. Macromolecules 2004, 37, 3071. c) Rizzo P, Spatola A, De Girolamo Del Mauro A, Guerra G. Macromolecules 2005, 38, 10089. d) Venditto, V.; De Girolamo Del Mauro, A.; Mensitieri, G.; Milano, G.; Musto, P.; Rizzo, P.; Guerra, G. Chem. Mater. 2006, 18, 2205.(4) (a) De Rosa, C.; Guerra, G.; Petraccone, V.; Pirozzi, B. Macromolecules 1997, 30, 4147. (b) Milano, G.; Venditto, V.; Guerra, G.; Cavallo, L.; Ciambelli, P.; Sannino, D. Chem. Mater. 2001, 13, 1506.(5) (a) Rizzo, P.; Daniel, C.; De Girolamo Del Mauro, A.; Guerra G. Chem. Mater. 2007, 19, 3864. (6)Daniel, C.; Alfano, D.; Venditto, V.; Cardea, S.; Reverchon, E.; Larobina, D.; Mensitieri, G.; Guerra, G. Adv. Mater. 2005, 17, 1515-1518. (7)(a) Mensitieri, G.; Venditto, V.; Guerra, G. Sensors and Actuators B 2003, 92, 255-261. (b) Giordano, M.; Russo, M.; Cusano, A.; Mensitieri, G.; Guerra,G. Sensors and Actuators B 2005, 109, 177-184. (8)Buono, A.; Rizzo, P.; Immediata, I.; Guerra, G. J.Am.Chem.Soc. 2007, 129, 10992-10993.(9)a) P. Stegmaier, A. De Girolamo Del Mauro, V. Venditto, G. Guerra, Adv. Mater. 2005, 17, 1166. b) C. D'Aniello, P. Musto, V. Venditto, G. Guerra, J. Mater. Chem . 2007, 17, 531. (10)a) V. Venditto, G. Milano, A. De Girolamo Del Mauro, G. Guerra, J. Mochizuki, H. Itagaki, Macromolecules 2005, 38, 3696. b) De Girolamo Del Mauro, A.; Carotenuto, M.; Venditto, V.; Petraccone, V.; Scoponi, M.; Guerra, G. Chem. Mater. 2007, 19, 6041.(11)C. Daniel, N. Galdi, T. Montefusco, G. Guerra Chem. Mater. 2007, 19, 3302-3308.

Engineering Plastics – Markets & Trends

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Engineering Plastics MarketsThe global plastics market has grown around 6 % over the last decades. Since 2000 the largest consumption of plastics is found in Asia (incl. Japan). This is also true for Engineering Plastics. However, because of the excellent innovation capabilities the European market for Polyamide still dominates the globe. The regional shift in markets during the last years has hit the US much stronger than Europe as businesses moved to the low cost countries in Asia, while in Europe the shift has a large intraregional aspect going from Western to Central and Eastern Europe.The activities at the K 2007 in Düsseldorf created continued expectations for growth in the plastics market through the next years based on the full order books of the machine manufacturers.New ChallengesThe challenges for plastic materials are clearly defined in the ongoing high raw material cost. This triggers more and more the discussion of bio based raw materials. In contrast, the utilization of oil for chemical production e.g. in Western Europe reaches only a level of 8%, while plastics all together make up for only around 4%. These facts do not seem to put the discussion on a rational basis. Business in Europe will get more complex under the new REACH legislation. Unclear is still the directive for recycled materials. The decision in China to ban plastic bags shows that the negative discussion about the environmental issues of plastics is by far not over despite of their clear positive contribution to the reduction of CO2 emissions.Material DevelopmentDuring the K show many new material developments were exhibited, the trend: more specialties. In principle, existing polymer blocks are engineered into new materials. The failed introduction of complete new polymers in the past show the limits, customer requirements for change over risks, lagging scale up effects to reduce the manufacturing cost, unacceptable returns. Nanotechnology helps to find solutions, many options in modifying materials to overcome existing barriers e.g. mechanical properties against flow behavior have been possible. Also, bio based polymers are already introduced or R&D is announced by almost every raw material producer. The economical, even more important the environmental feasibility needs to be proven yet. As to material laws, high speed elongation and the proper description of the material behavior has been improved tremendously. Today, simulation tools put plastics in very early competition with metal where feasibility of success needs to be proven before a prototype is made.Processing TechnologyIn the processing field, just common injection molding without added value seems not to be able to survive long-term in developed countries. Cost pressure leads to integra-ted systems. While in the past e.g. gas injection molding might have been an eye catcher the combination of gas with water and multiple materials, functional injection molding, in-line compounding and high precision molding and machines, miniaturi-zation, mechatronic integration to name a few seem to be the answer to fight low prices and the competition from the East.Production TechnologyPolymerization for engineering plastics follows the trend in commodities of scaling up to cut further costs. The latest example in the US shows a polyamide plant with a capacity of 120 Ktons per annum in a single train. There are limits to this trend concerning local market access, transportation costs and local content requirements. In compounding, while the same trend is seen, the limits are reached even earlier in production run size and the increasing requirement for more flexibility. A contradiction so far which could only be resolved with smaller compounding machines. The FutureThe plastics industry is innovative. The general outlook stays positive in the years to come. This positive expectation is boosted by the inherent energy efficiency of plastics in many applications. The cost pressure will remain as raw material prices will not decline. The fight for resources will increase, however, the main basis for the next decades in chemical production and thus plastics will be oil, gas and coal. In the next decade new solutions will be found, they need to prove themselves in niche areas before they become standard technology.

Challenges and Opportunities for Plastics in Sustainable Energy Scenarios

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Among the challenges and opportunities ahead for the plastics industry, increasing attention is paid to environmental matters. In addition to production and process related environmental protection measures, many of the environmental activities in the past have concentrated on issues related to plastics waste. However, a much wider perspective integrating economic, ecological, social and not least also technological aspects is now emerging and termed “Sustainable Development”, and many efforts of the plastics industry are directed towards a positive contribution. A continuous shift towards Sustainable Development will not only significantly affect the polymer industry but also technology development in general and thus the industry and society as a whole.In this regard it is increasingly acknowledged that the transformation of the current fossil fuel based energy system to an energy system substantially to fully based on renewable resources in the mid- and long-term is at the core of a “true” sustainable energy scenario. While there are many open issues and problems to be resolved (also technologically) over the next decades to support such a transformation process, it is also clear that the transformation towards a future sustainable energy scenario will need to follow two basic guiding principles:(1)Continuous and significant enhancement in energy efficiency for all energy services(i.e., significant reduction in the energy intensity per service unit), and(2)Continuous increase in the use of renewable energy resources by implementing an adequate and optimized mix of available technologies.Regarding the above guiding principle (1), plastics and polymer based composites have proven in many instances that they contribute significantly to energy savings in a wide variety of applications (e.g., plastic foams for the thermal insulation of buildings, refrigerators etc., weight reduction in vehicles). And yet, there is still a huge potential for further innovations.As to guiding principle (2) it is certainly also true that polymeric materials are already in use for various solar energy components (e.g., glazings and transparent insulation, piping, thermal storage tanks, sealants and encapsulation materials). However, so far polymer engineering and science based innovative concepts have not yet been considered adequately in product development and applications of solar energy components and systems. Thus, particularly in this field there is an enormous potential for future innovations. These include polymeric materials for solar-thermal applications (novel polymeric glazing materials, thermotropic solar control materials, improved transparent insulation materials, polymeric solar absorber and heat exchanger materials) and solar-electrical applications (organic solar cells and new encapsulation materials). Moreover, as evidenced in the past by developments in numerous industrial sectors (e.g., electrics and electronics, automotive and aviation, general machinery, building and construction, packaging) a high potential for innovative advancements by the proper integration of polymeric materials is also to be expected for solar components and systems. Due to the wide range of properties that may be realized by polymeric materials combined with their cost efficient and highly flexible processability and the high potential or multi-functional integration, the advantages related to the use of polymers in solar components and systems include functional improvements, systems cost reductions and - last but not the least - more design freedom to meet the esthetic demands of architects and end-users. Finally, as a result of their property profile which may be tailored to specific requirements and applications together with their low density (light weight), polymeric materials ""use less to do more"", thus in this case too contributing to resource preservation.In the presentation various options and the role of polymeric materials in contributing to the transformation of the energy system towards the increasing utilization of renewable energy resources, in particular of solar energy, will be explored, providing numerous examples on the innovative use of plastics in this context.

Processing Polyimide Composites: A Review

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Since the 1950s, considerable progress has been made in the research and development of a wide variety of polyimides. Polyimides can be classified as thermosetting or thermoplastic polyimides. The former are generally easier to process but are more brittle than the latter. When the thermosetting and thermoplastic polyimides are combined, this results in a semi-interpenetrating polyimide which offers improved toughness. Prior work focused primarily on the performance of polyimides to meet military and aerospace application requirements. However, in recent years, there has been increasing commercial interest in using polyimides that are lightweight and can withstand high heat, while maintaining high mechanical strength. The commercial applications require the development of low cost processing methodologies because the fabrication cost comprises 70 to 90 percent of the total cost for a finished polyimide composite part. The 5-membered imide rings in a wholly aromatic polyimide are rigid, which imparts thermo-oxidative stability, but also causes high melt viscosity. The high melt viscosity requires a high cure temperature and high pressure for processing a polyimide matrix composite. Autoclave and compression molding have traditionally been the standard processing methods. More recently, several low cost processing techniques have been developed. These new, low cost processes include Resin-Transfer-Molding (RTM), Vacuum-Assisted-Resin-Transfer Molding (VARTM), and Double-Vacuum-Bag Vacuum-Assisted-Resin-Transfer Molding (DVBVARTM). Each of these processes has several variants. Selection of an appropriate processing methodology requires a fundamental understanding of the relationships between the processing conditions, chemistry, rheology, and properties of polyimides. This lecture presents results from the standard autoclave and compression molding of polyimides, as well as the newer lower cost processing techniques referenced above. The variables that factored into the selection of the appropriate processing methods for these materials will also be discussed.

The Solidification of Blends Containing Crystallizable Polymers: Opportunities to Control Morphology and Properties

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The blending and crystallization of inexpensive or ecologically useful polymers can provide pathways to a multitude of morphologies. It would be expected that this rich abundance of structures would provide materials with unique or useful properties. The pathways toward tailoring morphologies include (1) partial or complete liquid phase separation before crystallization and (2) control of kinetics and mass balances during crystallization. For the first case, amazingly little research has been performed, although what has been done has demonstrated the large potential in this area. In the second case, it is shown that the Peclet number for crystallization is an important controlling parameter. Examples of the range of morphologies available are given. In this case, possible outcomes are biphasic spherulites, interpenetrating spherulites, and the separation of components at a macroscale. Within these possibilities, the structures can be fine-tuned. Overall, what is currently known concerning morphological development is only a small fraction of what is possible, and this is even more true of the correlation of morphologies and properties. The entire area is seen as one of great opportunity to inexpensively tailor polymeric materials toward optimal properties.

Fiber processing supported with micro-structure analysis Usefulness of morphology snapshot technology

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A development of new production process is essential for a development of new polymer products. Needless to say, a molecular structure (one-dimensional structure) plays dominant role to determine the material characteristics. Furthermore a morphological control (three-dimensional structure) is required to achieve high functionality for a new polymer product. In order to achieve required morphology, the specification of production process itself should be designed based on the exactly required process conditions. For example, on a coagulation process for wet spinning, a phase diagram of spinning dope dramatically changes during the coagulation bath. On the beginning and on the end of coagulation process, the fiber bundle requires different conditions of coagulant, respectively. In order to understand exactly required conditions on a production process, a morphology snapshot technology (MST) is very useful because the changes of morphology during the process even in very short time can be analyzed. In our group, many trials on MST have been done by the use of transmission electron micrograph (TEM), X-ray scattering (XRS) by synchrotron radiation and light scattering (LS). Based on our experiences, the usefulness of MST ether on-line or off-line manner is discussed in this paper.Our first attempt of MST started as an off-line manner on the development of Ultra high molecular weight polyethylene (HMW-PE) strong fiber (Dyneema). The generation and deformation of shish-kebab structure on the production process was a key morphological issue. Using an off-line MST with TEM, we understood that the shish-kebab deformation determined the strength of Dyneema. The highest fiber strength and the fastest manufacturing speed were achieved with the understanding of the scientific background on production process.As next attempt of MST, an on-line synchrotron XRS measurement on a neck-like deformation of Polyethyleneterephthalate (PET) high speed spinning was investigated with late Prof. Zachmann in 1991, in terms of crystallization phenomena of PET. This was our first trial of the use of synchrotron on-line measurement. On transient phenomena of continuous process, such as a neck-like deformation on melt spin-line, the time is able to convert to the distance from start point. Very short period transition phenomena can be observed with enough time resolution by this way even for XRS measurement. We convinced that synchrotron radiation is very powerful tool for on-line MST.After these experiences, the development of Poly-p-phenylenebenzobisoxazole (PBO) fiber (Zylon) was started. We applied MST as a powerful tool in order to understand the relation between morphology and strength of fiber. The molecular orientation measurement of PBO during air-gap on spin-line using synchrotron XRS told us the required process conditions for air-gap part and the off-line MST using TEM showed the required morphology for fiber strength and the required conditions for production processes. The strength of 5.7GPa was achieved with a commercially acceptable manufacturing process. Furthermore the MST on the coagulation process using synchrotron XRS proved the reasonableness of the coagulation process which was developed based on the hypothesis of very shot period phase separation type coagulation.A scientific understanding on a production process shows an industrial process development the right direction. A MST is very powerful tool for development on the functional new product. Especially current new technologies, such as extremely strong light sources and very high S/N ratio probes, make MST more practical. New horizon of process development assisted by MST for polymer engineers has opened now, I believe.