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## Novel polymer materials using sub and supercritical gases

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The traditional methods for polymer processing involve either high temperatures, necessary for melting or viscosity reduction or hazardous organic solvents and chlorofluorocarbons. Due to the undesirable environmental and biological impact of these solvents, intensive research is focused on seeking new and cleaner methods for the processing of polymers. Applying supercritical fluids for particle formation may overcome the drawbacks of conventional particle size reduction processes. Powders and composites with special characteristics can be produced. Several processes for formation and design of solid particles using dense gases are studied intensively. The unique thermo-dynamic and fluid-dynamic properties of SCFs can be used also for impregnation of solid particles for formation of solid powderous emulsions, particle coating, e.g., for formation of solids with unique properties for the use in different applications. For production of particles with micron and submicron size, several methods using supercritical fluids like RESS and GASR, GASP, SAS/PCA/SEDS, SAA, UNICARB™, VAMP™, PGSSTM are described in the literature. The basis of practically all processes is fundamental thermodynamic data for the system polymer/dense gas. An overview of methods for investigation of the thermodynamic properties of the binary systems by different methods is offered. Binary system of polyethylene glycol (PEG)/CO<sub>2</sub> as a model system to study the interactions of polymers with SCF at elevated pressures was taken under research. Behavior of polyethylene glycols (PEGs) with different molar masses (ranging from 1,000 g/mol do 100,000 g/mol in the binary systems with CO<sub>2</sub>) was analyzed. The external balance method was developed for determination of the solubility of gas into substrates which are soluble in CO<sub>2</sub> densities of CO<sub>2</sub> saturated solutions of polyethylene glycols were measured by a volumetric method, developed by the authors. Viscosities of CO<sub>2</sub> saturated solutions of polyethylene glycols at elevated pressures were measured by a method, also developed by the authors. Capillary rise method adapted to the measurement conditions and sample properties was applied to investigate the interfacial tension. In details PGSS™ (Particles from Gas Saturated Solutions) process co-invented by author of this manuscript (USP 6,056,791) for the formation and formulation fine particles will be presented. In this process melts, solutions, emulsion or suspensions are intensively mixed with compressed gas most frequently the gas is carbon dioxide. In PGSS™ process the substance or the mixture of substances to be powderized must be converted into a sprayable form by liquefaction/dissolution. This can be achieved by melting or/and dissolving of the substance or mixture of substances in a liquid solvent or by dispersing solids or liquids in a melt or solution and saturation of the melt/solution/dispersion with the gas. Thus, viscosity and surface tension is lowered to such extent that low and high viscous fluids can be sprayed in a nozzle forming fine droplets. Then the gas-containing solution is rapidly expanded in an expansion unit and the gas is evaporated. Due to the Joule-Thomson effect and/or the evaporation and the volume-expansion of the gas, the solution cools down below the solidification temperature of the solute and the supersaturation is extremely high. In this way, fine particles are obtained, where the morphology, particle size, particle size distribution and crystallinity (various polymorphs) can be adjusted with operating process parameters. The presentation gives also limited overview of applications of sub- and supercritical fluids as processing media for production of novel materials with special properties.

### Biography

Željko Knez is currently a Dean of Faculty of Chemistry and Chemical Engineering of University of Maribor and visiting professor at University of Zagreb. He graduated and obtain PhD from Maribor University. Subsequently he made research at University of Wageningen and University of Erlangen (Germany) in the field of separation processes. In the past he was vice and executive rector, he was member of executive board of European Federation of Chemical Engineering, he was head of WP "High pressure technologies" of EFCE from 2003 to 2010, he is member of several professional and scientific organizations. He is member of European Academy of Sciences and Arts. Publications include more than 170 articles presented in SCI journals, he give more than 600 presentations at different conferences has more than 2800 citations and "h" index 26. He is coauthor of 15 patents and patent applications and his is coauthor of 14 books published by Taylor and Francis, Wiley, Woodhead Pub., Elsevier, etc.

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