Supercritical Fluid Dispersions in Polymerisations and Coatings

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Solvent choice in polymer manufacture and processing is dictated by a number of factors, but is increasingly concerned with meeting ever more stringent environmental controls on solvent emissions. While increasing use of water as a solvent in polymer production and use meets some of the requirements, it is not without its own problems. This has led in the last 10 years to a substantial interest in the use of supercritical fluids, particularly supercritical carbon dioxide ($scCO_2$), as solvents in polymer processes. Solubility requirements mean that much of the evolving technology surrounding the use of $scCO_2$ involves the use of colloidal dispersions and aerosols. There are two main polymer processes where use of $scCO_2$ is likely to make a significant impact in future – these are (a) polymerisation reactions, and (b) coating processes. The science of these processes and their relevance to polymer colloids will be reviewed in this talk.

Polymerisation processes

$ScCO_2$ is a poor solvent for most polymers other than siloxanes and amorphous fluoropolymers. As a result, much research activity has focussed on the study of dispersion polymerisation reactions, where the key is the design of specific stabiliser molecules containing both 'polymer-philic' and 'CO_2-philic' structures. While the use of amphipathic macromolecules (block or graft copolymers or *in situ* graft copolymers) can be effective, shorter chain molecules can also be highly efficient when a specific interaction can occur between the growing polymer particle and the stabiliser head group. Steric stabilisation prevents aggregation and coalescence of the particles. Examples of dispersion polymerisation in carbon dioxide will be presented, including use of fluorocarbon and siloxane macromonomers for methyl methacrylate polymerisation and copolymerisation, use of graft and block copolymers and use of shorter chain molecules. Most work has been carried out on acrylic polymers, but success has also been achieved with polystyrene and the principles have been extended to step growth polymerisation.

Polymer coatings

Although polymer coating technology is of considerable commercial importance and subject to relatively new EU legislation on emissions, the use of $scCO_2$ as a replacement solvent has been little studied to date. Spray coating processes such as the Unicarb™ process can permit replacement of the majority of the organic solvent in a coating system by CO_2. Of particular interest to us is the complete replacement of the organic solvent by using polymer dispersions in CO_2. This is virtually uncharted territory and could involve the use of dispersion polymers synthesised in CO_2 or the redispersion of polymer powders prepared by an alternative route. Issues which need to be understood include effects of equipment parameters (temperature/ pressure) and stabiliser structural parameters (*e.g.* molecular weight, block/graft length *etc.*) on the nature of the spray and its subsequent coating ability. Spray coating of aerosols has also been reported recently as a route to speciality inorganic oxide coatings and could be applied to polymer coatings.