A supercritical CO_2 process for the production of vinyl functionalised polymer particles

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Supercritical CO_2 ($scCO_2$) is a viable medium for producing microparticles via dispersion polymerisation processes[1]. The most common commercial use to date for $scCO_2$ has been in the selective extraction. This work exploits both of these processes to produce multifunctional microparticulate materials; core-shell microparticles with vinyl group surface functionalisation in a one-pot procedure. The most interesting aspect of these particles is the reactivity of their double bonds on the surface, which can be thermally activated post-synthesis to generate cross-linked materials. In principle allowing us to build strong tough coatings or 3-D materials.

We demonstrate here the use of $scCO_2$ system to synthesise microparticles relying on the selective extraction capabilities of the solvent. Implementation of a reversible addition-fragmentation chain transfer (RAFT) polymerisation allows for the selective polymerisation of one vinyl group in an asymmetric divinyl monomer (allyl methacrylate) (Figure 1) – thus generating a linear polymer with pendant vinyl groups. Dynamic mechanical analysis (DMA) has been employed to demonstrate the purely thermal curing of these materials as coatings, as well as the subsequent improvement in mechanical properties post cross-linking. The processing window for these materials has been shown to be modifiable by the copolymerisation of the shell with methyl methacrylate (MMA), allowing for the modification of both the curing temperature and thermal transitions of the polymers, while still retaining the desired functionality.

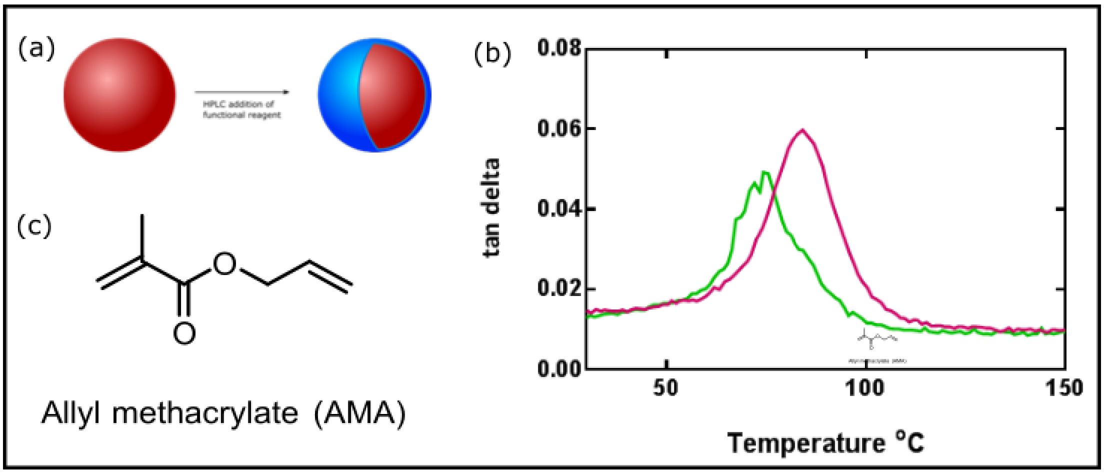

Figure 1. (a) Mechanism of the core-shell process, (b) DMA thermogram of the T_g increase after curing, showing pre-cure (green) and post-cure (purple), and (c) allyl methacrylate monomer

References

1 Gregory, A. M., Thurecht, K. J. & Howdle, S. M. Controlled dispersion polymerization of methyl methacrylate in supercritical carbon dioxide via RAFT. *Macromolecules* 41, 1215-1222 (2008).