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Microwave-assisted degradation of Polymers with Supercritical Carbon Dioxide for Plastic Recycling

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Advantages of microwave heating

- Microwaves heat materials volumetrically…

Figure 1- Schematic of volumetric heating (left) against conventional heating (right).

..where the core of the material is heated at the same rate as the surface, allowing high temperatures to be reached quickly.[1]

- Microwaves heat materials selectively…

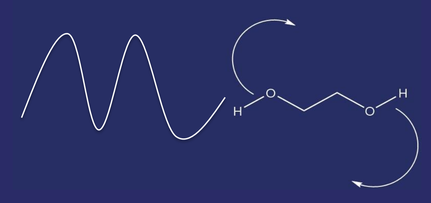


Figure 2- Schematic of the dipolar heating mechanism.

…as a permanent dipole, or free charge carriers, must be present for the electric field to induce heating in the material. [1]

Supercritical CO_2-induced plasticisation

- Carbon dioxide enters its supercritical state above its critical pressure (74 bar) and temperature (31.1 ° C).
- The ability of supercritical carbon dioxide to enhance polymer chain mobility has been extensively covered in the literature. [2]
- This process is known as plasticisation, and can commonly be identified by a reduction in a polymer's glass transition temperature (Fig 3).

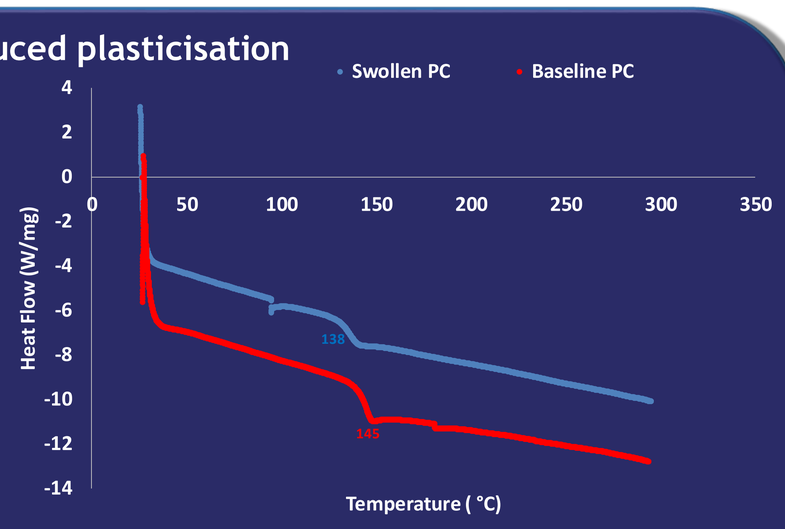


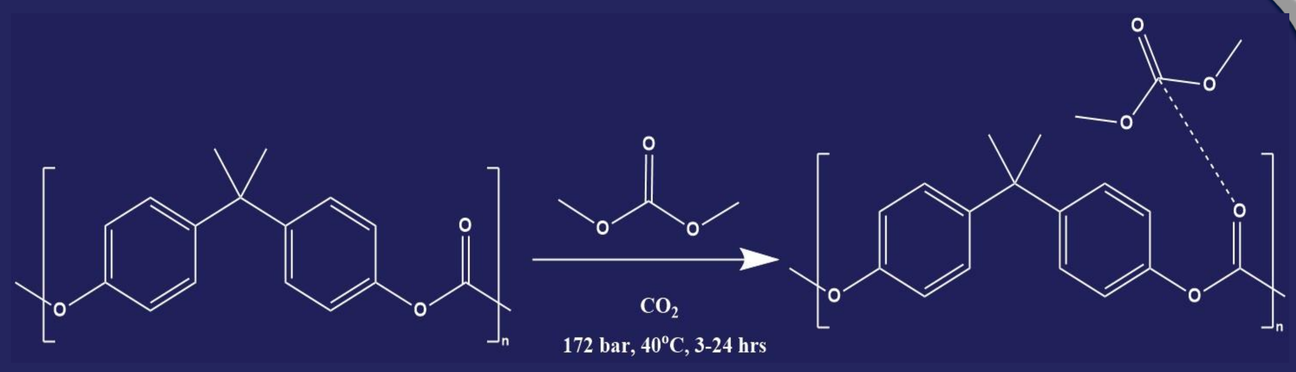
Figure 3- DSC curves of Bisphenol-A Polycarbonate before (red) and after (blue) soaking in $scCO_2$ for 18 hours at 209 bar. Glass transition temperatures are annotated.

Why combine these two technologies?

- Polymers are poorly heated by microwaves for two reasons:

1. They do not contain any free charge carriers e.g. ions, delocalised electrons.
2. They consist of very long chains, which can give rise to very stables structures. This limits the efficiency of the dipolar heating mechanism (Fig.2), as the chains are very resistant to motion induced by the alternating electric field.

- Supercritical carbon dioxide's ability to increase the mobility of the chains, and the premise of combining this green solvent with microwave heating is being explored to produce a quick, sustainable method of recycling plastics.
- Doping polymers with microwave susceptors can indirectly supply heat, but a critical drawback is the requirement to separate the susceptor from the pyrolysis products. [3]
- Current work is focussing on an efficient method for delivery of a microwave susceptor into a polymer matrix that will not require separation from the pyrolysis products (Scheme 1).



Scheme 1 – Range of conditions currently being employed for the impregnation of Bisphenol-A Polycarbonate with dimethyl carbonate in supercritical carbon dioxide.

Figure 4- Future guest molecule candidates for impregnation experiments, 2-phenyl ethanol (left) and ethylene glycol (right).

Measurements of impregnated Bisphenol-A Polycarbonate's dielectric properties

- Bisphenol-A polycarbonate was soaked in supercritical carbon dioxide, in the presence of dimethyl carbonate in a 1:1 molar ratio, at 172 bar and 40 ⁰C for 24 hours.
- The dielectric properties of polycarbonate impregnated with dimethyl carbonate can be calculated from cavity perturbation measurements, and used to determine the dielectric loss tangent.
- The dielectric loss tangent of the impregnated polycarbonate was compared to that of an unaltered sample (Fig 5).
- Below 150 ⁰C a clear enhancement of the loss tangent can be observed for the impregnated polycarbonate, which disappears at higher temperatures once the glass transition temperature of the polymer is exceeded (147 ⁰C).

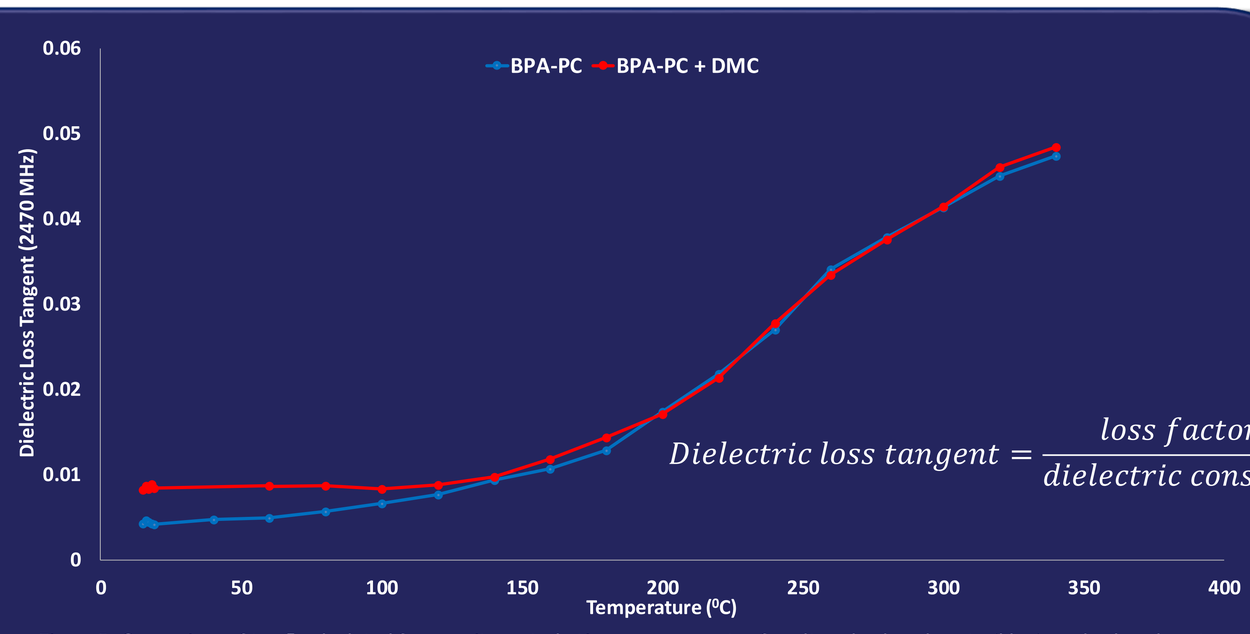


Figure 5- Comparison of tan δ calculated from cavity perturbation measurements of unaltered polycarbonate (blue), and polycarbonate impregnated with dimethyl carbonate (red).

References

1. R. C. Metaxas and R. J. Meredith, *Industrial Microwave Heating*, Peter Perengius Ltd, London, 3rd edn., 1993..
2. A. Naylor *et al*, *Advanced Materials*, 2008, **20**, 575–578.
3. H. Kitchen *et al*, *Chem.Rev*, 2014, **114**, 1170–1206.

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