

SURFACE PERCOLATION OF PROTONS A PROBE FOR THE CREATION OF CRYSTAL DEFECTS IN LACTOSE MONOHYDRATE FOLLOWING SHORT MILLING TIMES

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INTRODUCTION The aim of present work is to elucidate the mechanisms of dielectric relaxation of ball-milled lactose.

METHOD Lactose monohydrate (EP) was used in this study. The sieved sample (with size approximately $\geq 180 \mu\text{m}$) was ball milled for various time intervals (15, 45, 90 min at 40% RH) and thermal analysis was performed using TGA and DSC immediately after each stage of milling. Dielectric measurements were also taken immediately post milling using a Solartron 1296/1255 dielectric spectrometer across the frequency range 0.1-10⁶ Hz at discrete temperatures from -80 to 100 °C at 5 °C increments (the chamber of the cryostat was maintained at 0% RH during the measurement).

RESULTS The dielectric properties for the pre-milled sample, in the frequency and temperature domains (data not shown), has a simple response surface with a single percolation peak (which has been ascribed previously to the percolation of protons in the hydration surface of the particles). At 15 min of milling (and beyond) a second percolation peak appears (Figure 1) at higher temperatures than the original. At this time point, both peaks are significantly higher than that for pre-milled sample, presumably because water, which is released on disrupting the α -lactose monohydrate, now adsorbs onto the partially amorphized surfaces of fractured particles. This appears to increase, dramatically, both the number and size of percolation induced dipoles (as evidenced by an increase in the percolation peak height). At 45 min, the magnitude of the percolation process has reduced again, presumably because the high temperature of the mill has driven off much of the surface water in the sample. Both percolation peak temperatures increase up to 90 min of milling but whereas the first peak decreases thereafter, as the milling time extends beyond 90 min, the second percolation process disappears. This observation is co-incident with the observation that the particles are close to reaching their limiting size of 90 nm.

DISCUSSION An increase in percolation temperature suggests an effective increase in the scale length of the percolation path (Gorbatschow, Arndt et al. 1996). It follows that the changes in either percolation peak might be ascribed to one of two mechanisms:

(i) The creation of (more tortuous) internal paths for proton conduction that result from the creation of nano-scale defects in the crystal lattice and/or micro-scale defects such

as fissures within individual particles (these are observable in SEM images at short milling times).

(ii) Milling is known to produce both an amorphous surface phase while converting a proportion of α -lactose to β -lactose (Shariare, de Matas et al. 2011). It might be the case that the effective scale length of the percolation path increases as the protons are forced to migrate through the amorphous surface domains in order to reach the grain boundaries of the particles.

Given that the second percolation peak effectively disappears once the particles have been reduced to a certain limiting size, we might suggest that the origin of second percolation peak can be ascribed to mechanism (1), i.e. the creation of micron-scale defects.

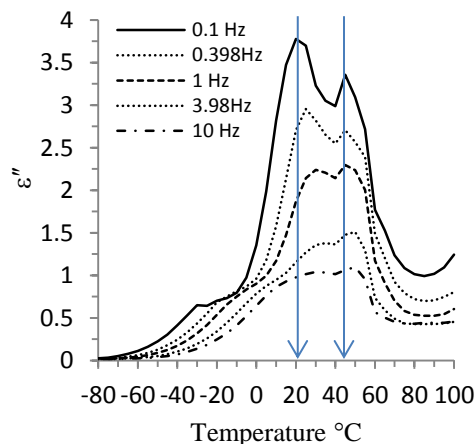


Figure 1: Temperature slices in dielectric spectra of crystalline lactose showing imaginary part of permittivity plotted against temperature in sample after 45 minute milling.

CONCLUSION

Aside from the obvious increase in surface area, and hence increased dissolution rate that results from size reduction, this data presents evidence for the creation of additional contributing factors, such as defects in the crystal lattice of lactose which are manifest in the formation of amorphous surface phase and fissures within particles.

REFERENCES

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