Electronic Supplementary Material (ESI) for RSC Advances.

Textural characterisations of modified starches

Gelatinisation and retrogradation were used to open up the granular structure of starch and to increase its surface area, i.e. expansion. SEM analysis showed that textural changes of the granule surfaces had taken place after the modification process as can be seen in Fig. 1S A-B. Native high amylose corn starch granules possess different granule shapes, ranging from spherical-, oval- or rod-like. The surface of the granules was smooth without obvious pores or fissures. After gelatinisation and retrogradation, the morphology of starch granules dramatically changed. Gelatinised starch (Fig. 1S C-D) and retrograded starch (Fig. 1S E-F) granules showed porous texture. In addition, the gelatinised and retrograded starch particles show irregularity in their size and shape, resulting from swelling and possible amylose migration during gelatinisation.

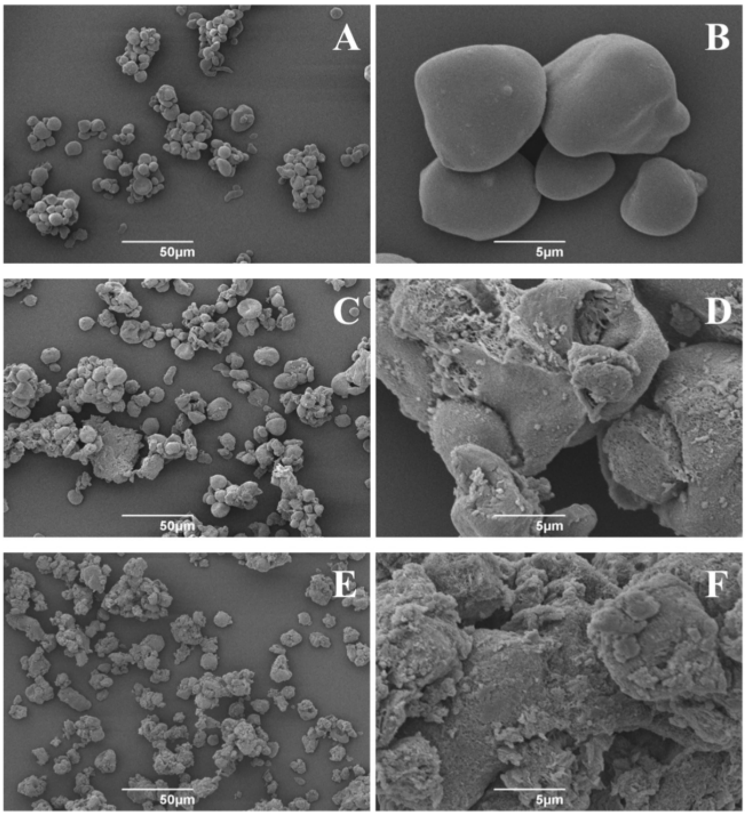


Figure 1S - Scanning election micrographs (magnification ×500 and ×5000) of native high amylose corn starch (A, B), gelatinised high amylose corn starch (C, D) and retrograded high amylose corn starch (E, F)

Thermal decomposition of starch and modified starches

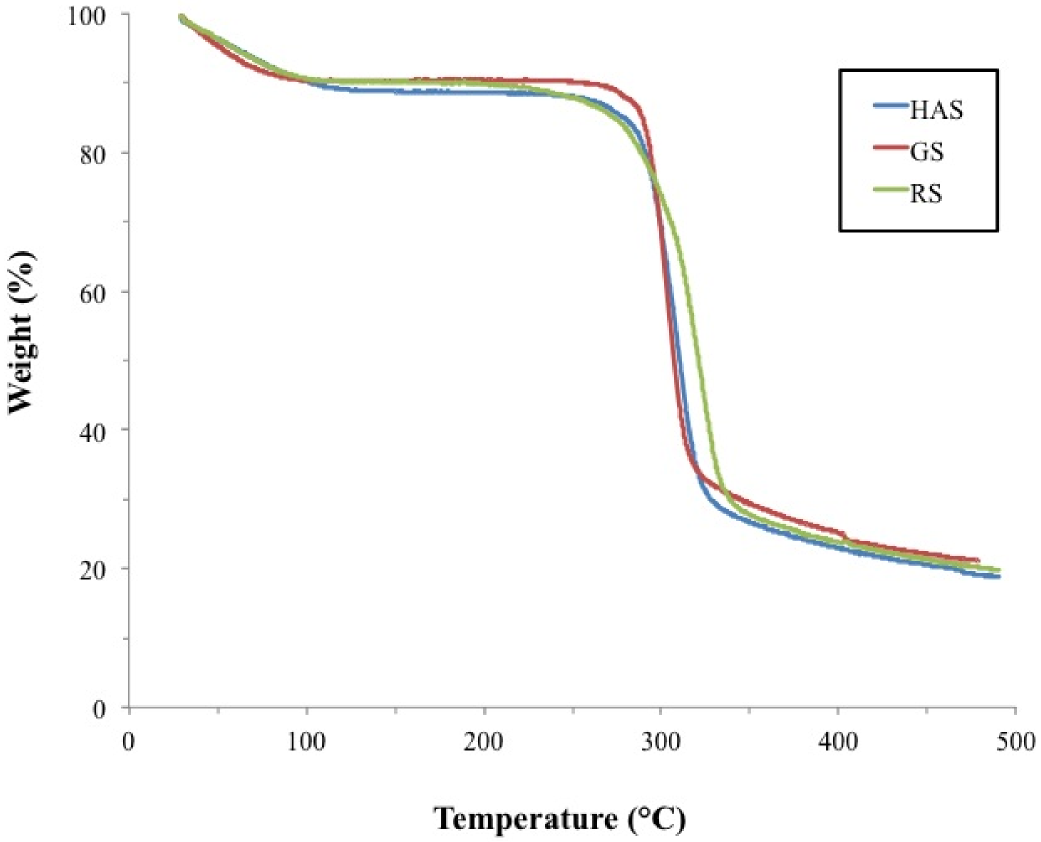


Figure S2 – TGA thermograms of unmodified (HAS), gelatinised (GS) and retrograded high amylose corn starches (RS)

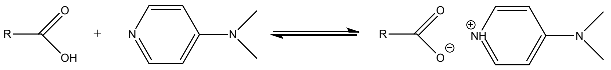
The decomposition temperatures of all samples are assigned by determining the peak temperature of dTG traces and summarised in Table S1. The decomposition temperatures of all starch samples are comparable, however the retrograded starch shows a slightly higher temperature of degradation relative to the other starches.

The chemical reactions occurring during the thermal decomposition of starch were studied by Zhang *et al.* using ^{13}C high solution solid-state NMR spectroscopy.[1] Thermal condensation and dehydration occur around 300 °C to generate ether and ethylene segments. At higher temperatures, aromatic rings such as phenol/benzene and furan structures are formed with methylene and ether linkages. A similar observation was reported by White *et al.* with expanded starch samples, however in this case, the decomposition occurs at lower temperatures.[2]

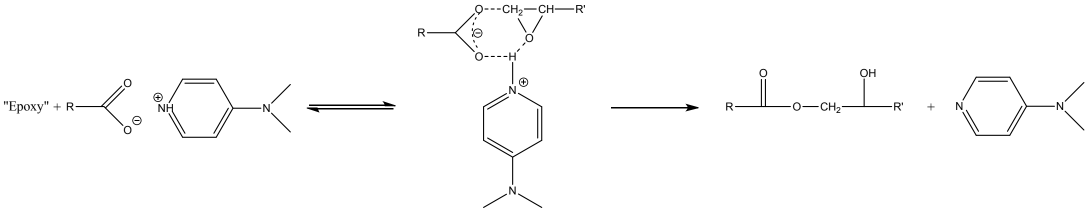
Table S1 – Thermal characteristics of native, gelatinised and retrograded starches

Starch type	**Weight loss (%) (150-500 °C)**	**Decomposition temperature (°C) (dTG peak)**
HAS	70.9	316.4
GS	69.3	314.9
RS	70.6	323.0

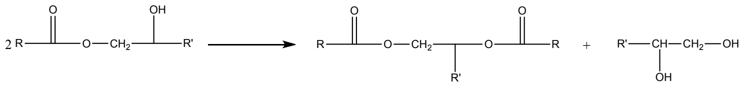
Mechanistic study of the system



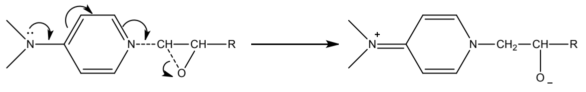
(1)



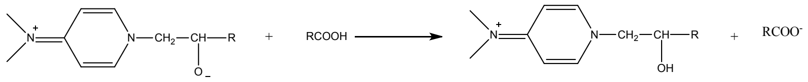
(2)



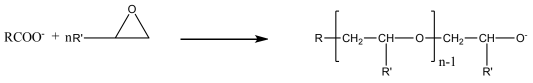
(3)



(4)



(5)



(6)

Figure S3 - Proposed reaction mechanism between “epoxy” and carboxylic acid in the presence of DMAP

Based on the literature and by analogy, the following mechanism may be proposed as outlined in Fig. S3. The main reaction is the epoxy-carboxylic acid addition esterification reaction, i.e., steps (1) and (2), followed by transesterification of the generated ester groups (step (3)). Alternatively, if DMAP acts a nucleophile promoting ring opening of the epoxide then steps (4) – (6) are conceivable.

Thermal properties of the composites

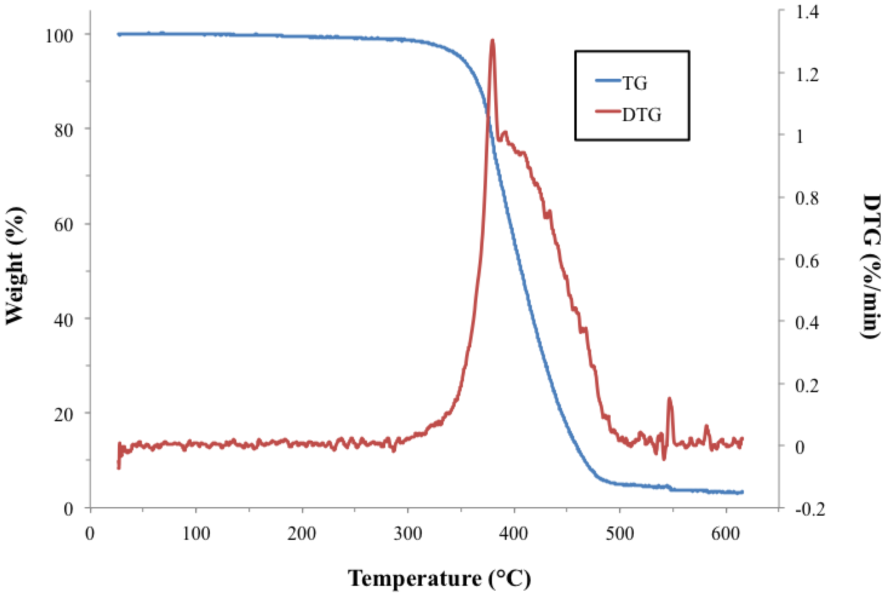


Figure S4 – TG and dTG curves of epoxidised linseed oil (25-625°C, 10 °C/min)

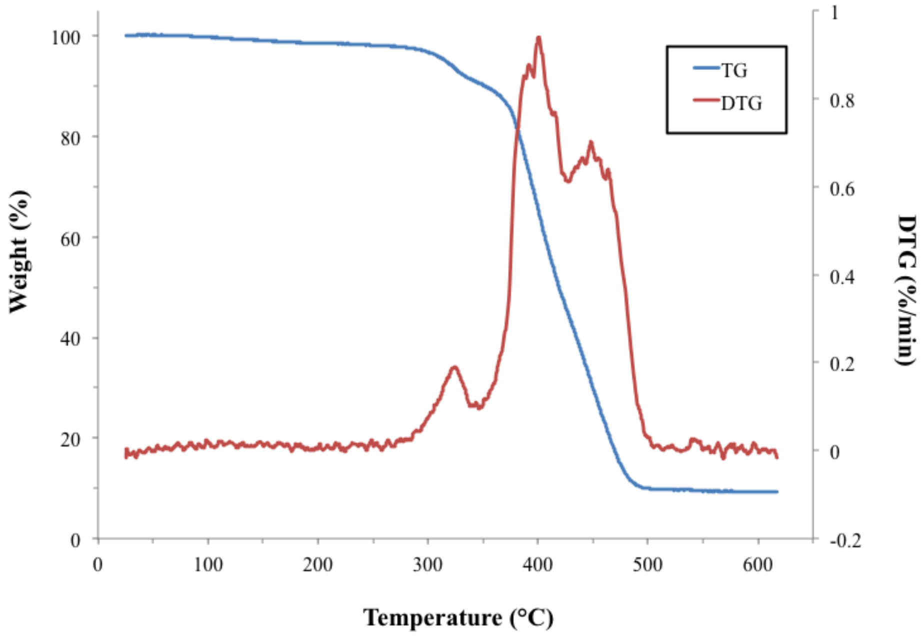


Figure S5 – TG and dTG curves of film with native high amylose corn starch (25-625°C, 10 °C/min)

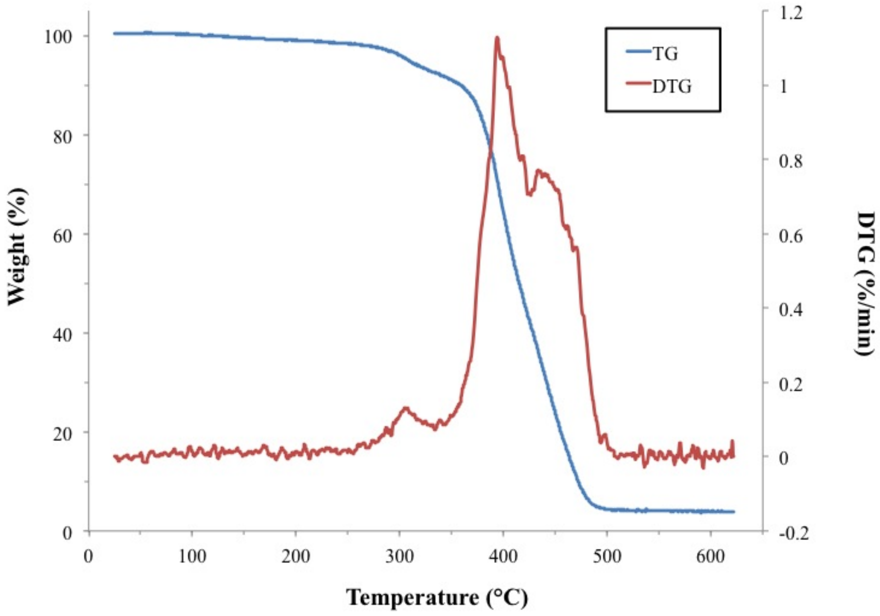


Figure S6 – TG and dTG curves of film with gelatinised high amylose starch (25-625°C, 10 °C/min)

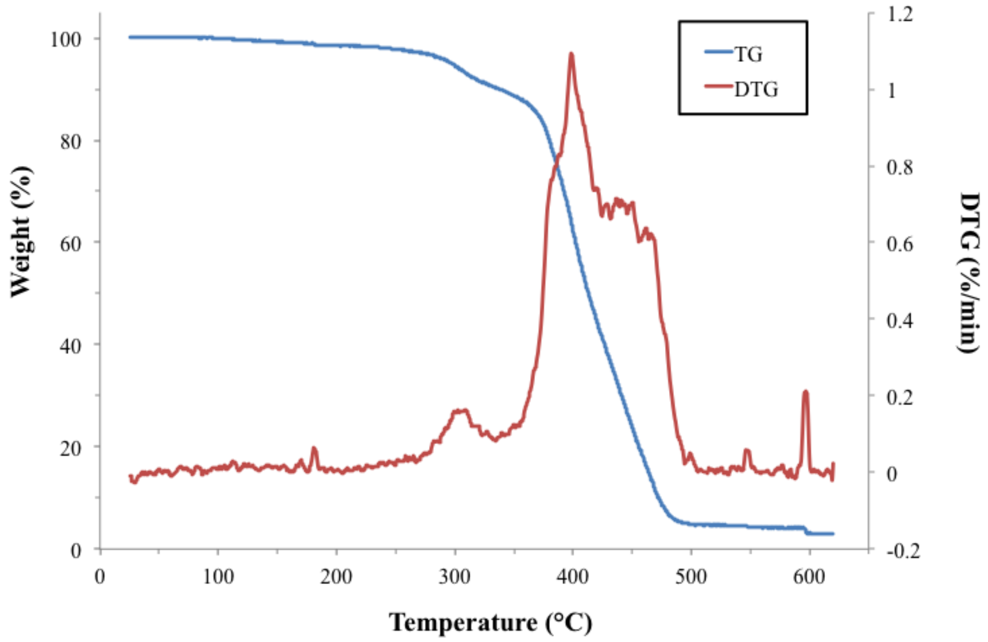


Figure S7 – TG and dTG curves of film with retrograded high amylose starch (25-625°C, 10 °C/min)

Curing study by infrared spectroscopy

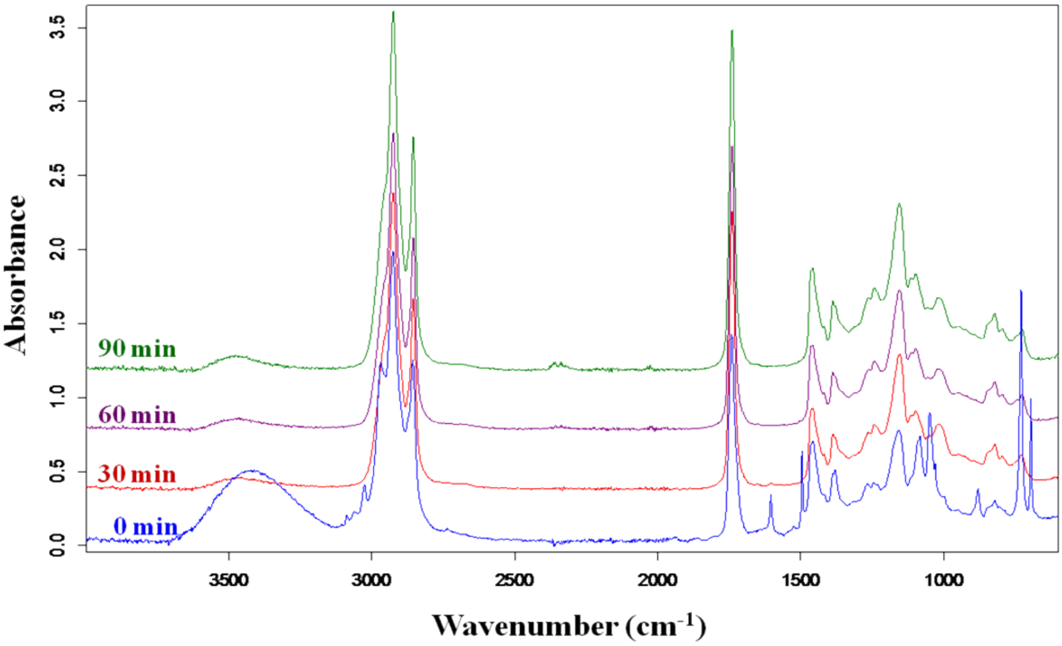


Figure S8 – Infrared spectra of ELO and expanded starch mixture (0.5% of total weight DMAP catalyst) cured at 140 °C

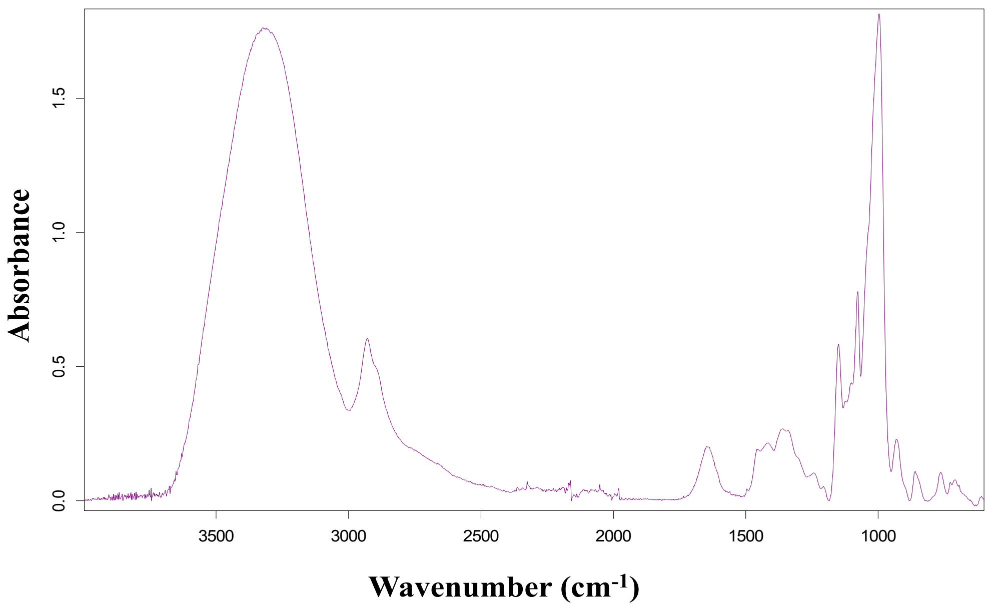


Figure S9 – Infrared spectrum of dried expanded starch

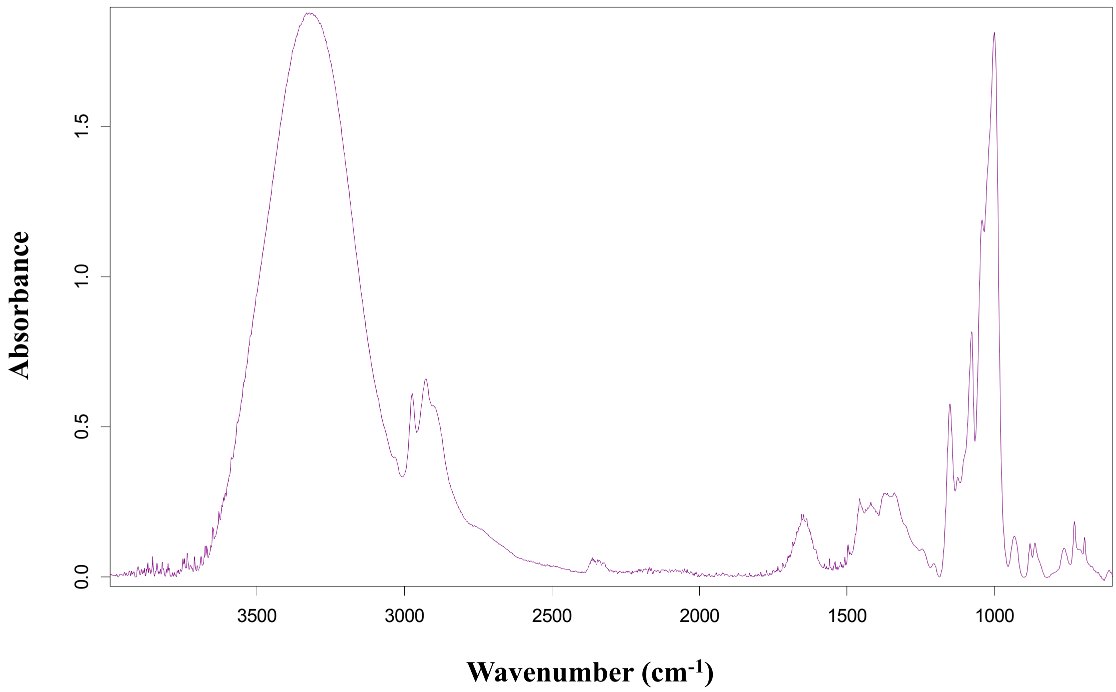


Figure S10 – Infrared spectrum of expanded starch in toluene

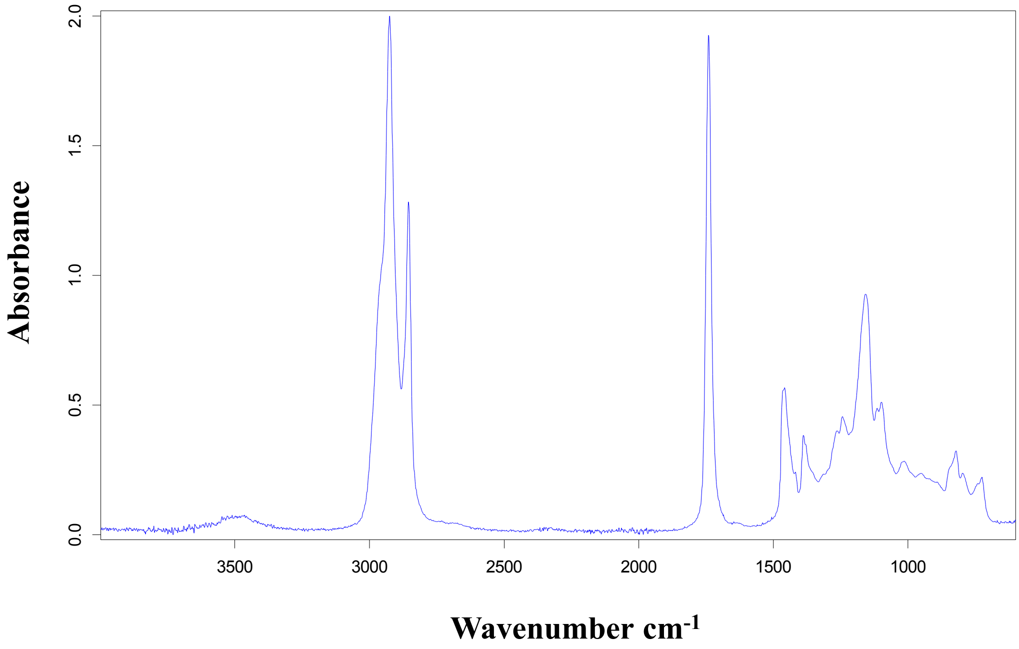


Figure S11 – Infrared spectrum of epoxidised linseed oil

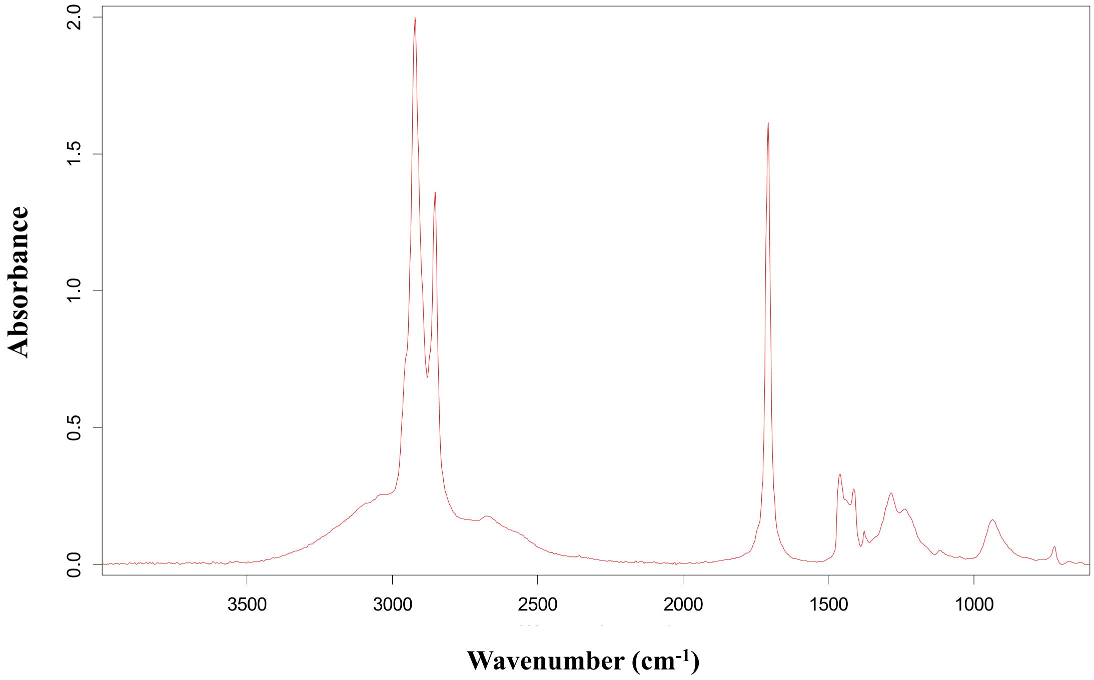


Figure S12 – Infrared spectrum of Pripol

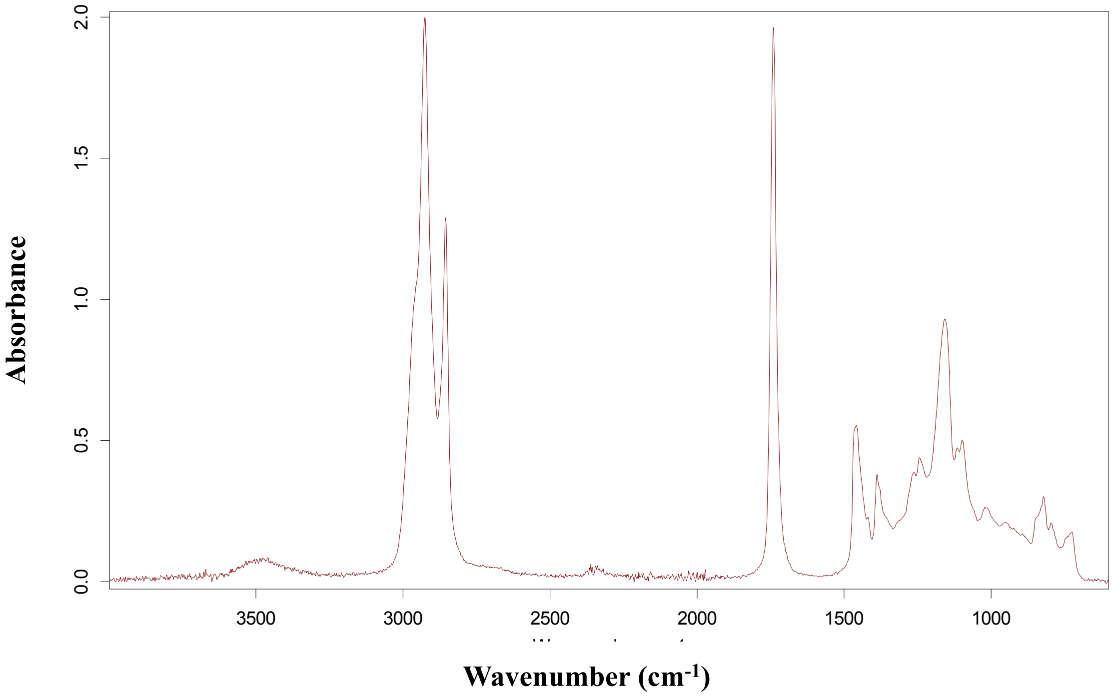


Figure S13 – Infrared spectrum of homopolymerisation of ELO in the presence of DMAP

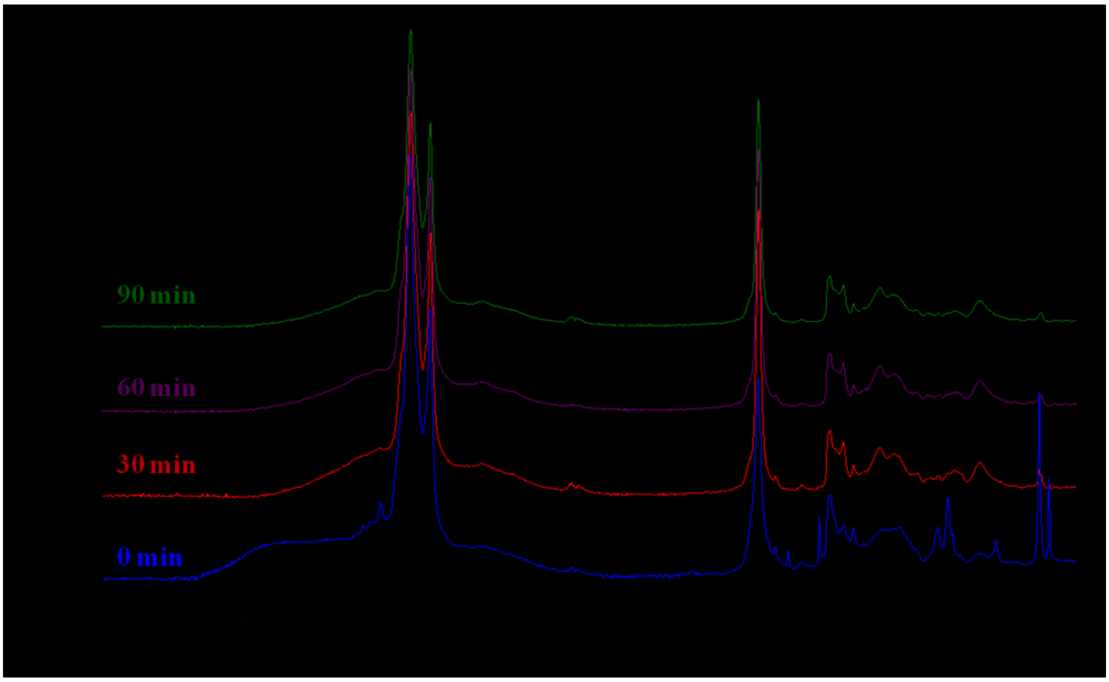


Figure S14 – Infrared spectra of Pripol and expanded starch mixture (0.5% of total weight DMAP catalyst) cured at 140 °C

References

1. X. Zhang, J. Golding and I. Burgar, *Polymer*, 2002, 43, 5791-5796.
2. R. J. White, V. Budarin, R. Luque, J. H. Clark and D. J. Macquarrie, *Chem. Soc. Rev.*, 2009, 38, 3401-3418.