# Supporting Information

# Green and sustainable devulcanization of ground tire rubber using choline chloride-urea deep eutectic solvent

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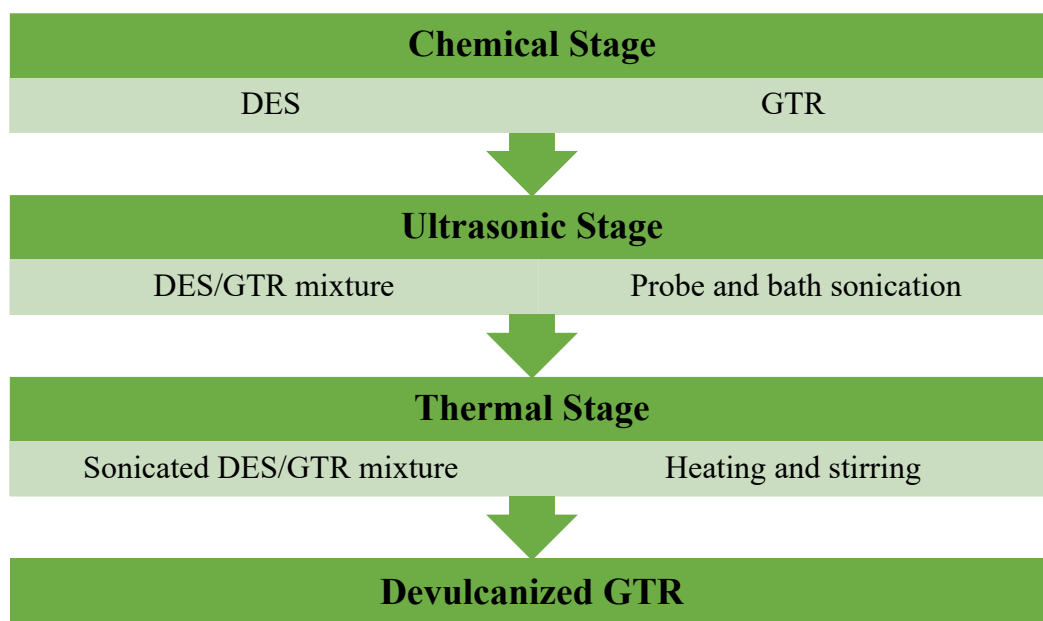
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# 1 Preparation of the DES

In this study, a green DES were prepared to devulcanize the GTR. The solvent consisted of choline chloride and urea (ChCl-urea) with a molar ratio of 1:2. DES was prepared according to the method used by Saputra et al. [1, 2]. ChCl and urea were mixed inside a glass beaker using a 3 cm magnetic stirrer while being heated at 80 °C using a hotplate. Deep eutectic solvents (DESs) have special properties that allow them to melt at a far lower temperature than their constituents, choline chloride (ChCl) and urea, which have melting points above 80 °C. The solvent was stored in a Schott bottle after obtaining a clear liquid with no solids inside. After closing the lid, the bottle was sealed with Parafilm to minimise the chance of crystallization resulting from moisture uptake by the solvent [2]. To minimise the water absorption by the solvent, DES was prepared just before the devulcanization procedure and used in a matter of minutes.



Figure 1. Prepared DES, a viscous, colourless, and clear solvent

| **Chemical Stage** | |
|---|---|
| DES | GTR |

↓

| **Ultrasonic Stage** | |
|---|---|
| DES/GTR mixture | Probe and bath sonication |

↓

| **Thermal Stage** | |
|---|---|
| Sonicated DES/GTR mixture | Heating and stirring |

↓

| **Devulcanized GTR** |
|---|

Scheme 1. Schematic diagram of the devulcanization procedure used in this work.

## 2 Flory-Rehner analysis

Before calculations, the samples were extracted according to ASTM D6814 and by using the Soxhlet extraction method [3]. In this procedure, 0.2 g of each rubber sample was measured and placed in a 500-mesh woven wire pouch. Then the pouch was placed in the extraction apparatus, and extraction was performed using toluene at 120 °C for 72 hours. The solvent was refreshed every 24 hours.

The same amount of rubber was measured and placed in a 500-mesh woven wire pouch. The pouch was placed in a beaker filled with toluene for 72 hours, and the solvent was refreshed every 24 hours. This was done to calculate the samples' solvent uptake and swelling degree. After 72 hours, the samples from the Soxhlet extractor and beakers were pat-dried quickly to remove the excess solvent and weighed. In the next step, samples were dried in an oven at 80 °C for 24 hours, and their weight was measured again.

Measurements showed that the density of the untreated rubbers is 1.16 g cm$^{-3}$, which agrees with the material data sheet provided by the producer. The density of the devulcanized samples was measured as 1.095 g cm$^{-3}$.

The swelling degree (Q – Eq. 1) shows the dimensional change in the rubber after absorbing the solvent and reaching an equilibrium.

$$Q = \frac{M_t - M_1}{M_1} \times 100 \tag{1}$$

In this equation, $M_t$ and $M_1$ are the mass of swollen devulcanized rubber and the mass of devulcanized rubber before swelling.

Soluble fraction (S – Eq. 2) gives a good understanding of the chains that are not linked to other chains and can be removed from the polymer. This parameter can be calculated after the Soxhlet extraction.

$$S = \frac{M_1 - M_2}{M_1} \tag{2}$$

In (Eq. 2), $M_2$ is the mass of the devulcanized rubber after it is dried.

One of the most important parts of the Flory-Rehner equation is calculating the term $V_r$ which is the volume fraction of polymer in a swollen network in equilibrium with pure solvent. The following equation is used to calculate $V_r$:

$$V_r = \frac{Weight\ of\ dry\ rubber/Density\ of\ dry\ rubber}{\frac{Weight\ of\ dry\ rubber}{Density\ of\ dry\ rubber} + \frac{Weight\ of\ absorbed\ solvent}{Density\ of\ solvent}} \qquad (3)$$

Another important parameter is $\chi$ or the Flory-Huggins polymer-solvent interaction parameter. This dimensionless parameter can be calculated using the following equation [1, 2]:

$$\chi = 0.429 + 0.218 V_r \qquad (4)$$

Crosslink density ($\nu$) can be calculated by using the available parameters and replacing them in the following equation:

$$\nu = \frac{\ln(1 - V_r) + \chi V_r^2 + V_r}{V_s(\frac{V_r}{2} - \sqrt[3]{V_r})} \qquad (5)$$

In (Eq. 5), $V_s$ is the molar volume of the solvent used for Soxhlet extraction which in this study was toluene (0.867 g cm$^{-3}$).

Finally, the devulcanization percentage (%Dev) can be calculated using the following formula:

$$\%Dev = (1 - \frac{\nu_f}{\nu_i}) \times 100 \qquad (6)$$

As mentioned earlier, the density of crosslinks before and after devulcanization are shown with $\nu_i$ and $\nu_f$, respectively. Table 7 shows the calculated Q, S, and %Dev for each sample.

Table 7. Calculated Q, S, and %Dev parameters

| Rubber sample | Q (%) | S (%) | %Dev. |
|---|---|---|---|
| S.F$_u$ | 49.77 | 15 | - |
| 40 M$_u$ | 50.41 | 11 | - |
| 80 M$_u$ | 55.09 | 10.8 | - |
| 120 M$_u$ | 50.12 | 8.2 | - |
| S.F$_{dv}$ | 56.71 | 3.07 | 29.3 |
| 40 M$_{dv}$ | 57.68 | 3.45 | 42.1 |
| 80 M$_{dv}$ | 67.48 | 3.00 | 51.48 |
| 120 M$_{dv}$ | 75.66 | 4.09 | 58.13 |

# 3 Horikx analysis

To investigate the successful devulcanization of rubber, the Horikx analysis can be used [1, 4, 5]. This analysis relates the sol fraction of the devulcanized rubber to the reduction in terms of crosslink density. Horikx theory provides a relationship between the soluble content generated as a result of degradation and the relative reduction of crosslink density caused by crosslink or chain scission. In the case of backbone (C-C bonds) scission, the relative reduction of crosslink density can be calculated using the following equation [2, 5, 6]:

$$1 - \frac{\nu_f}{\nu_i} = 1 - \left[ \frac{(1 - s_f^{\frac{2}{2}})^2}{(1 - s_i^{\frac{2}{2}})^2} \right]^{\frac{1}{2}} \quad (7)$$

Here, $S_i$, $S_f$, $\nu_f$, and $\nu_i$ are soluble fractions of untreated rubber, soluble fraction of devulcanized rubber, crosslink density of untreated rubber, and crosslink density of devulcanized rubber, respectively. In the case of selective crosslink scission, where the procedure selectively breaks the C-S bonds, the above equation should be corrected using two coefficients that were defined by Verbuggen [1, 6, 7].

$$1 - \frac{\nu_f}{\nu_i} = 1 - \left[ \frac{\gamma_f(1 - s_f^{\frac{2}{2}})^2}{\gamma_i(1 - s_i^{\frac{2}{2}})^2} \right]^{\frac{1}{2}} \quad (8)$$

In (Eq. 8), $\gamma_i$ and $\gamma_f$ are the average number of crosslinks per chain in the insoluble network before and after devulcanization. By plotting equations 7 and 8, the broken bonds during the devulcanization process and the selective, random, or degradative scission scenarios can be identified.
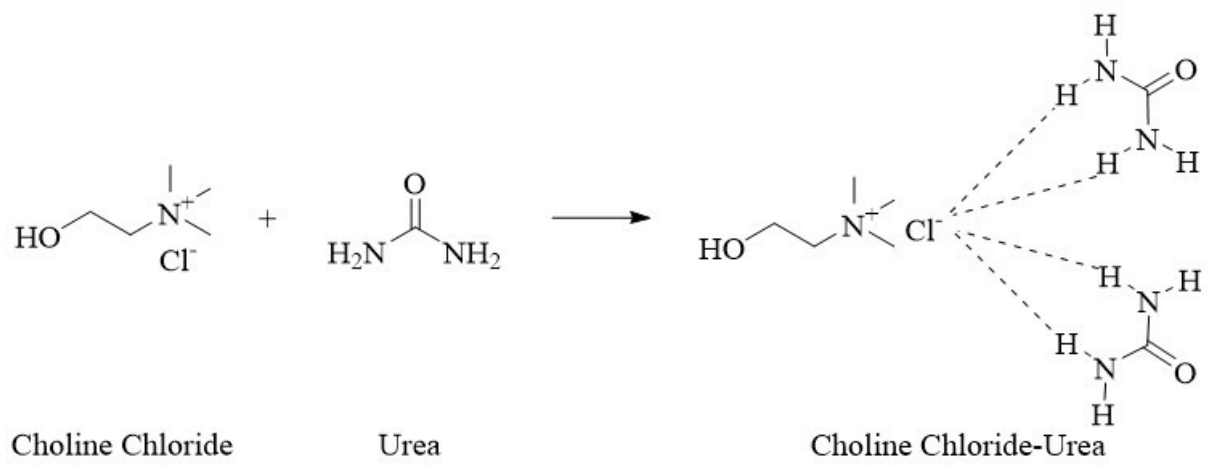
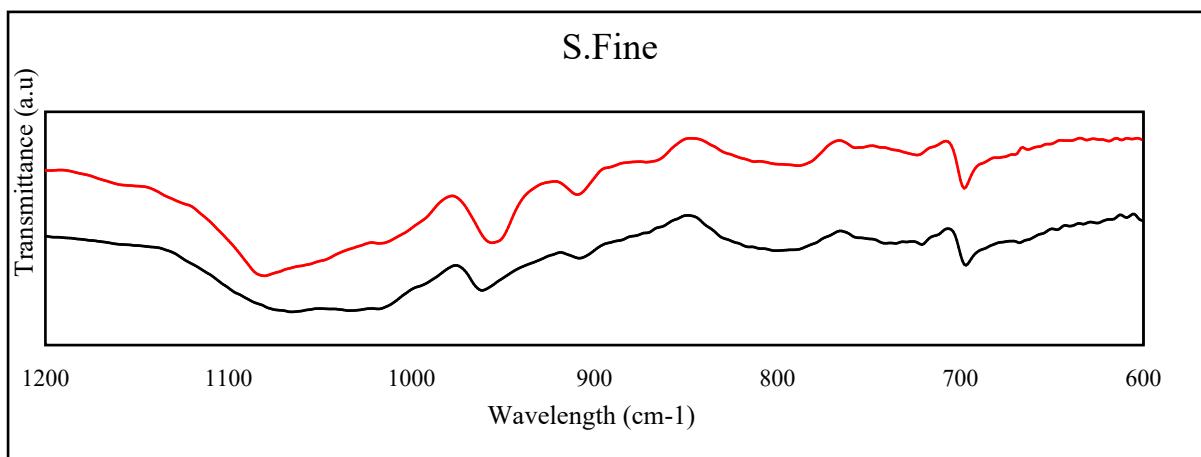Figure 2. The chemical reaction between choline chloride and urea

Figure 3. ATR-FTIR spectra of S.F$_{dv}$ sample, the black line belongs to untreated and the red line belongs to the devulcanized rubber
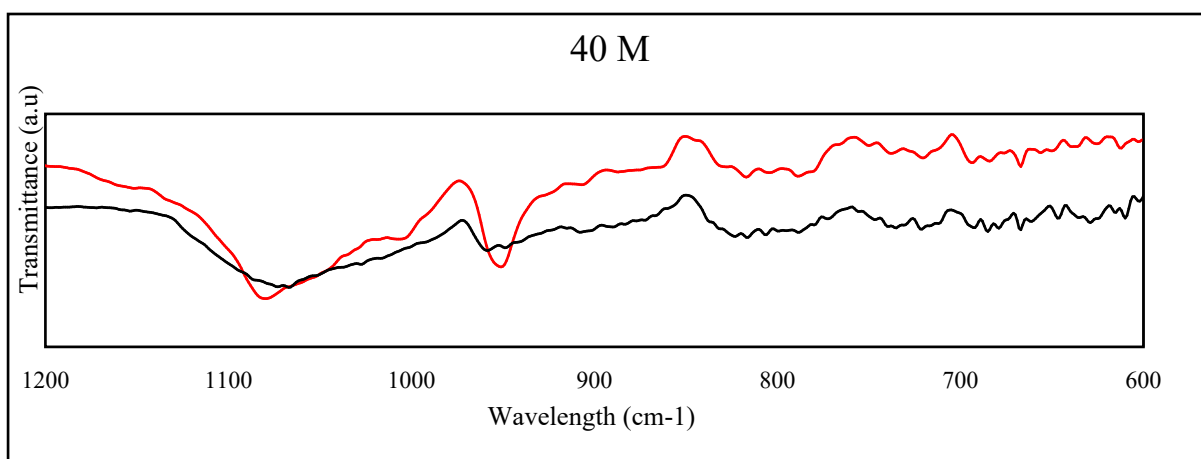


Figure 4. ATR-FTIR spectra of 40 M$_{dv}$ sample, the black line belongs to untreated and the red line belongs to the devulcanized rubber
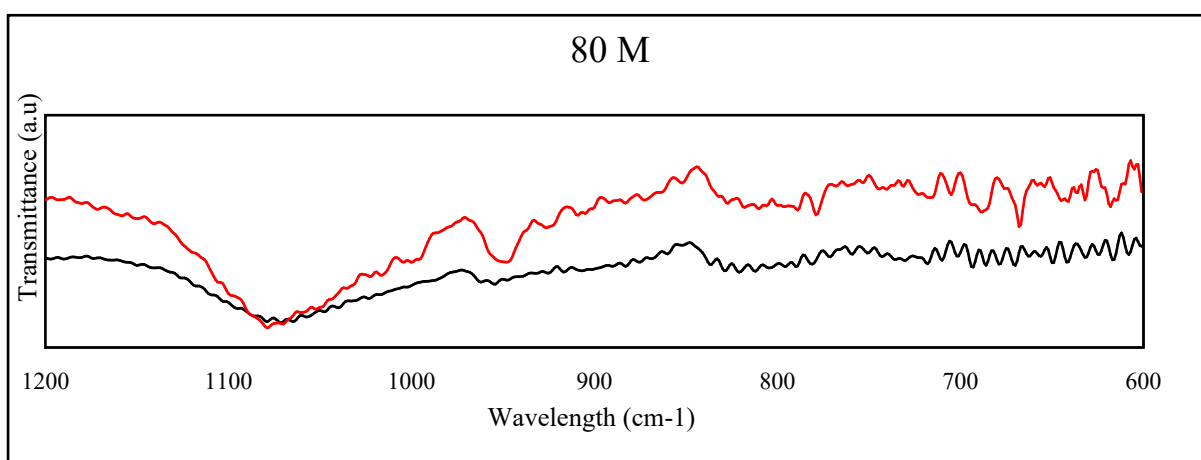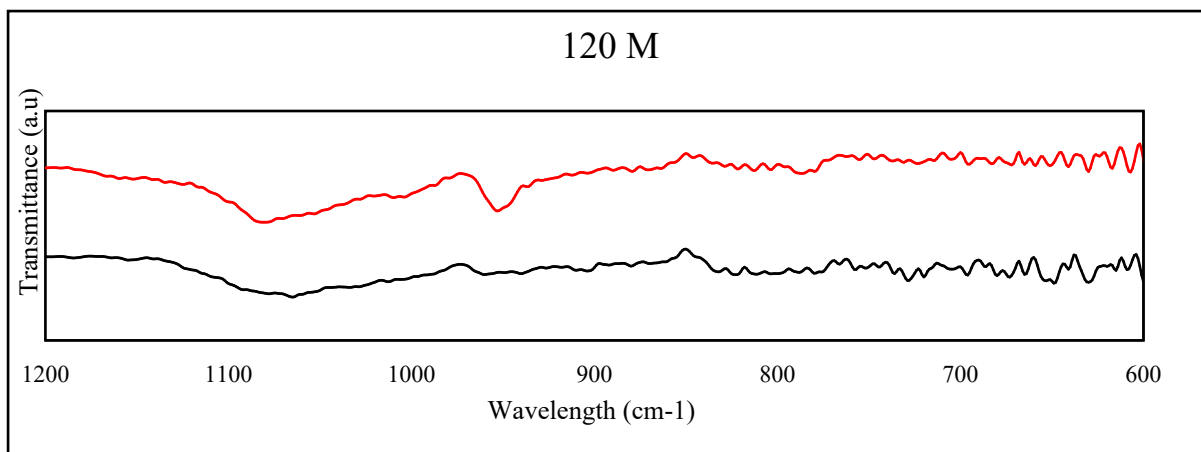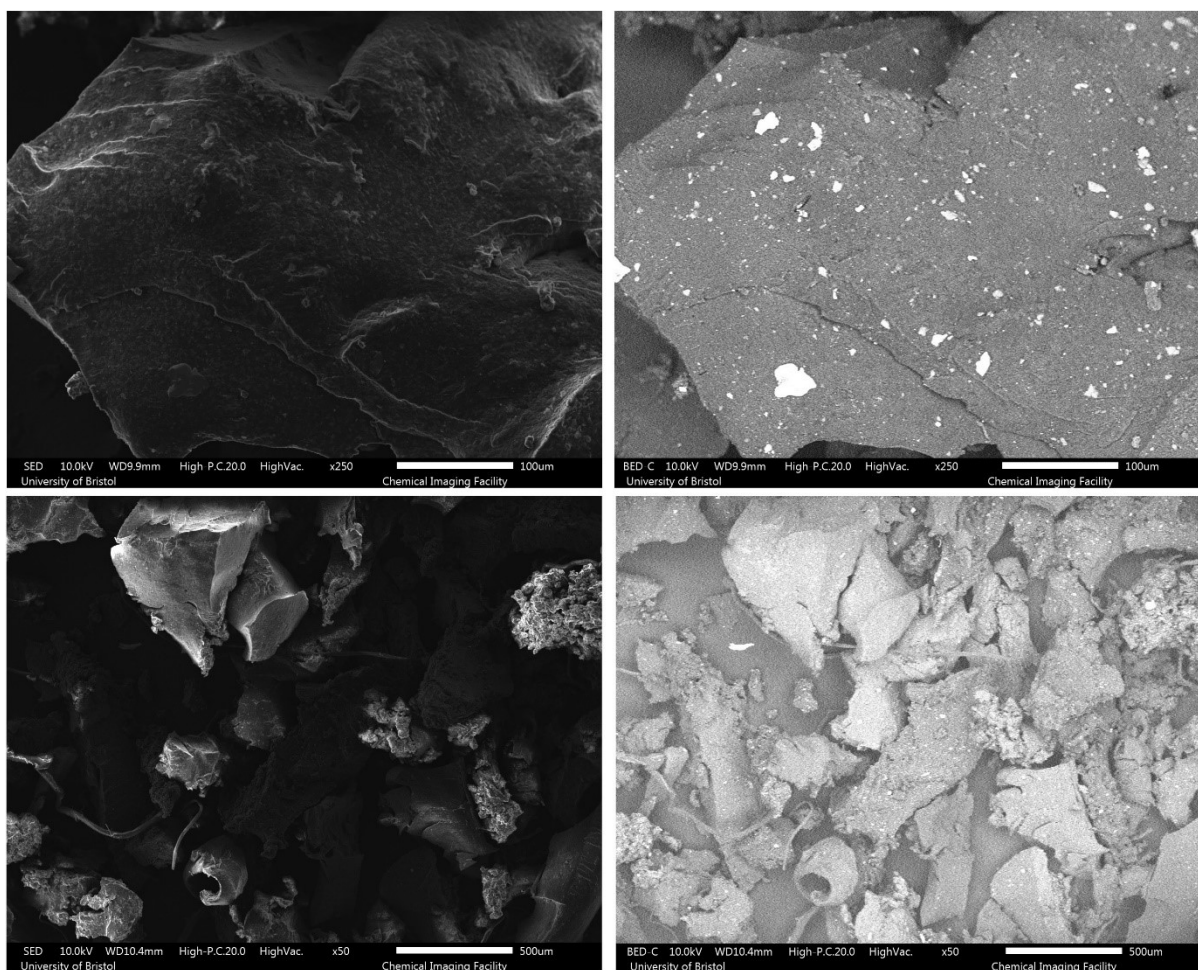


Figure 5. ATR-FTIR spectra of 80 M$_{dv}$ sample, the black line belongs to untreated and the red line belongs to the devulcanized rubber

Figure 6. ATR-FTIR spectra of 120 M$_{dv}$ sample, the black line belongs to untreated and the red line belongs to the devulcanized rubber

Figure 7. Different magnifications of S.F$_u$, left column: SED and right column: BED
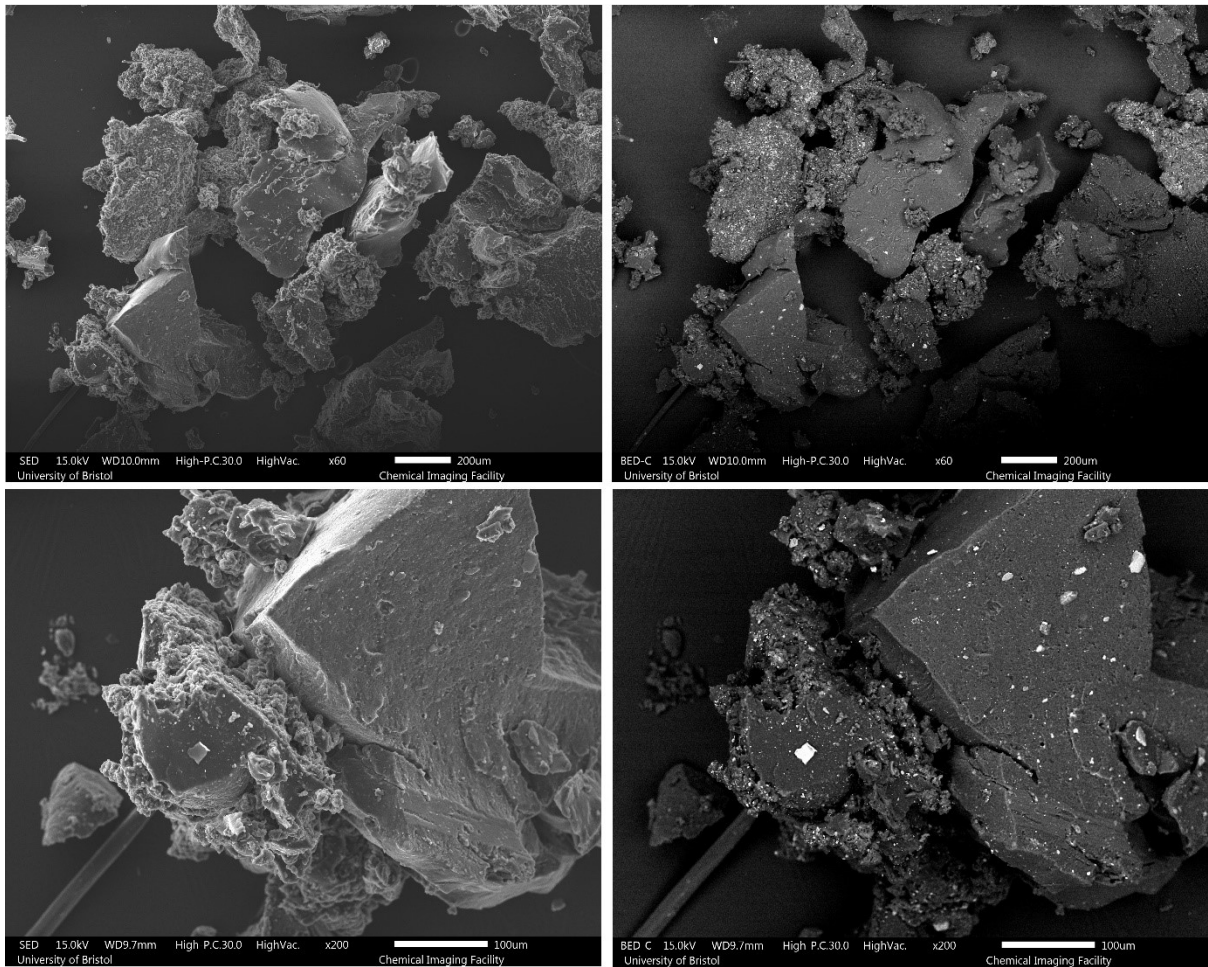
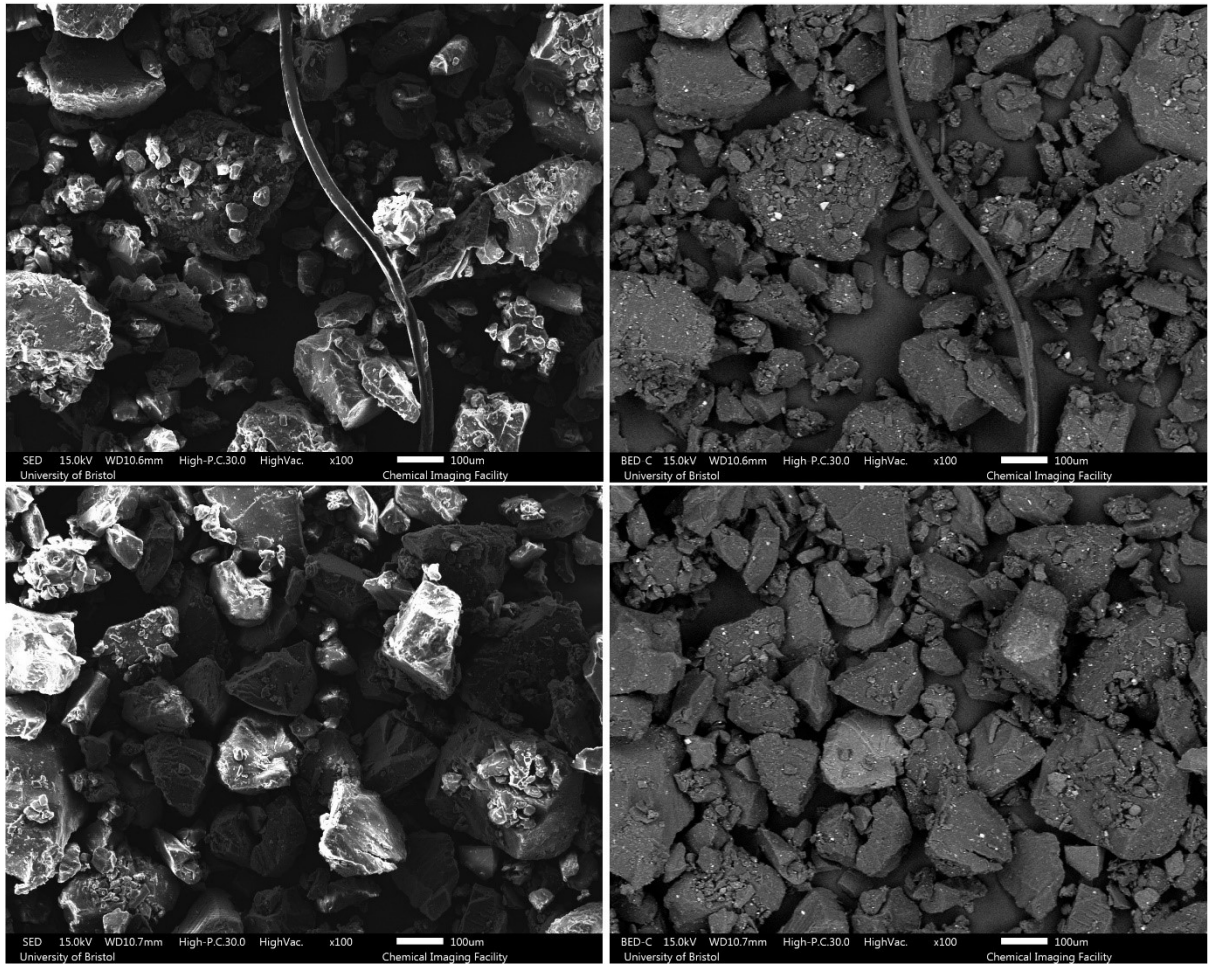Figure 8. Different magnifications of S.F$_{dv}$, left column: SED and right column: BED

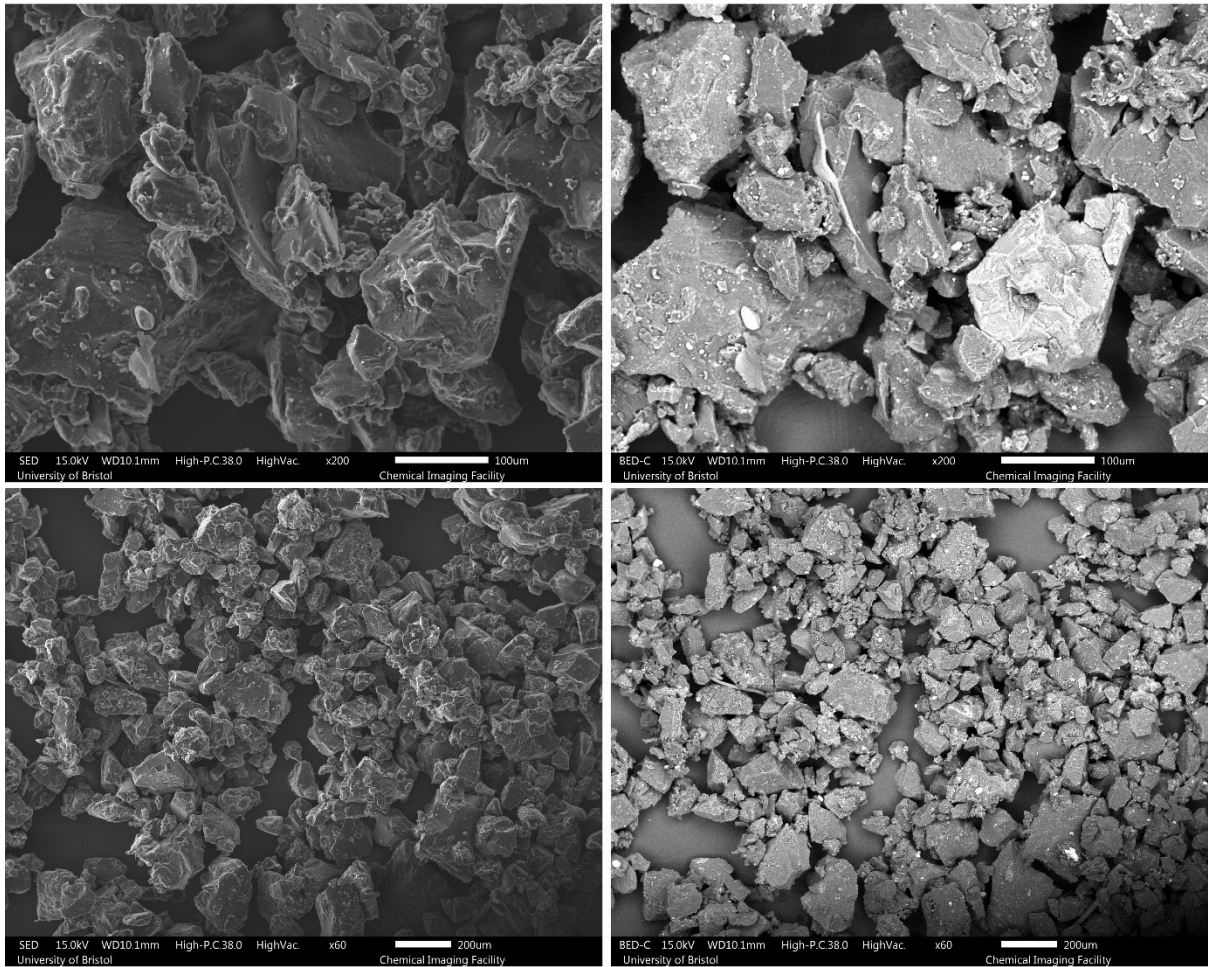Figure 9. Different magnifications of 40 $M_u$, left column: SED and right column: BED

Figure 10. Different magnifications of 40 $M_{dv}$ left column: SED and right column: BED
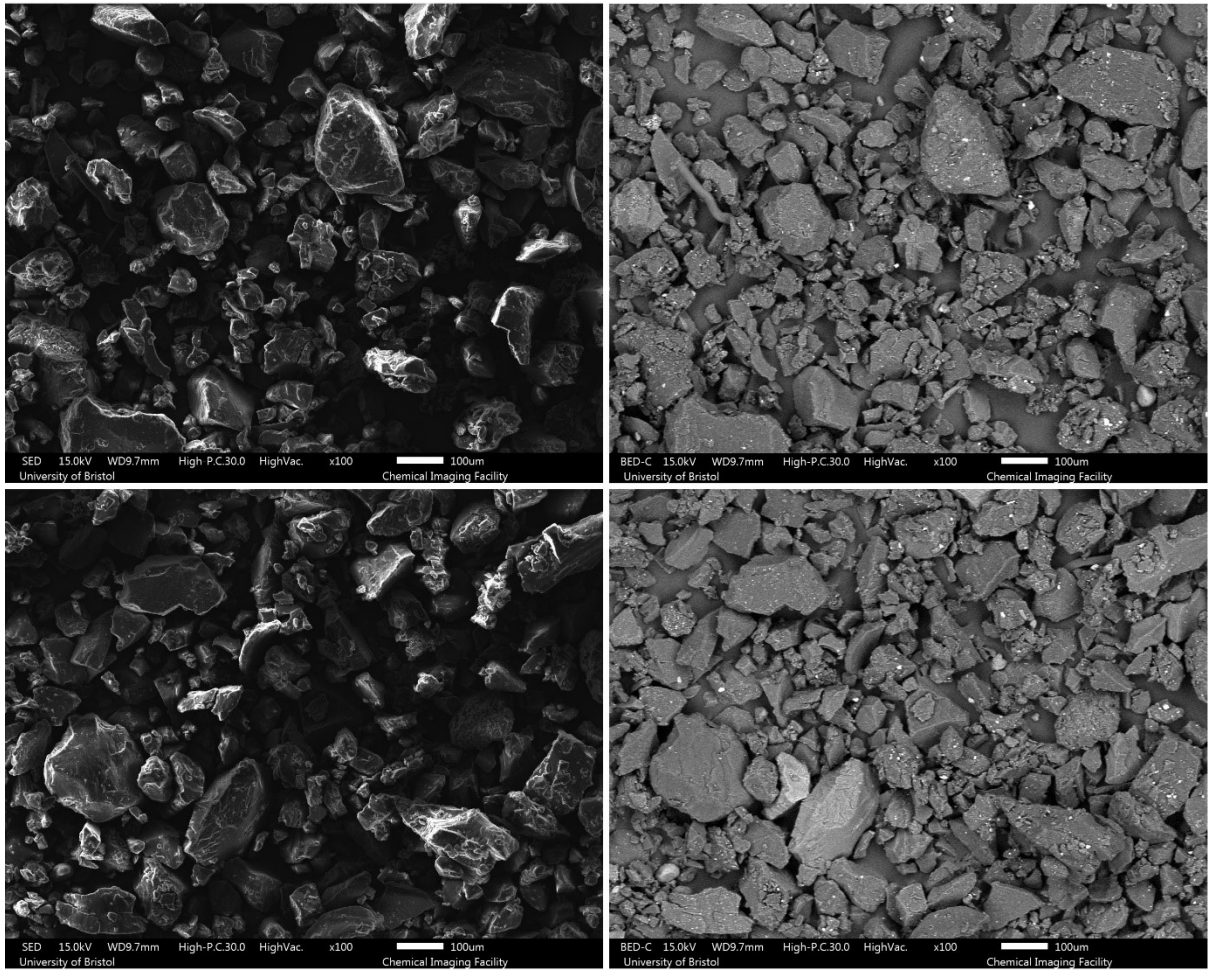
Figure 11. Different magnifications of 80 $M_u$, left column: SED and right column: BED
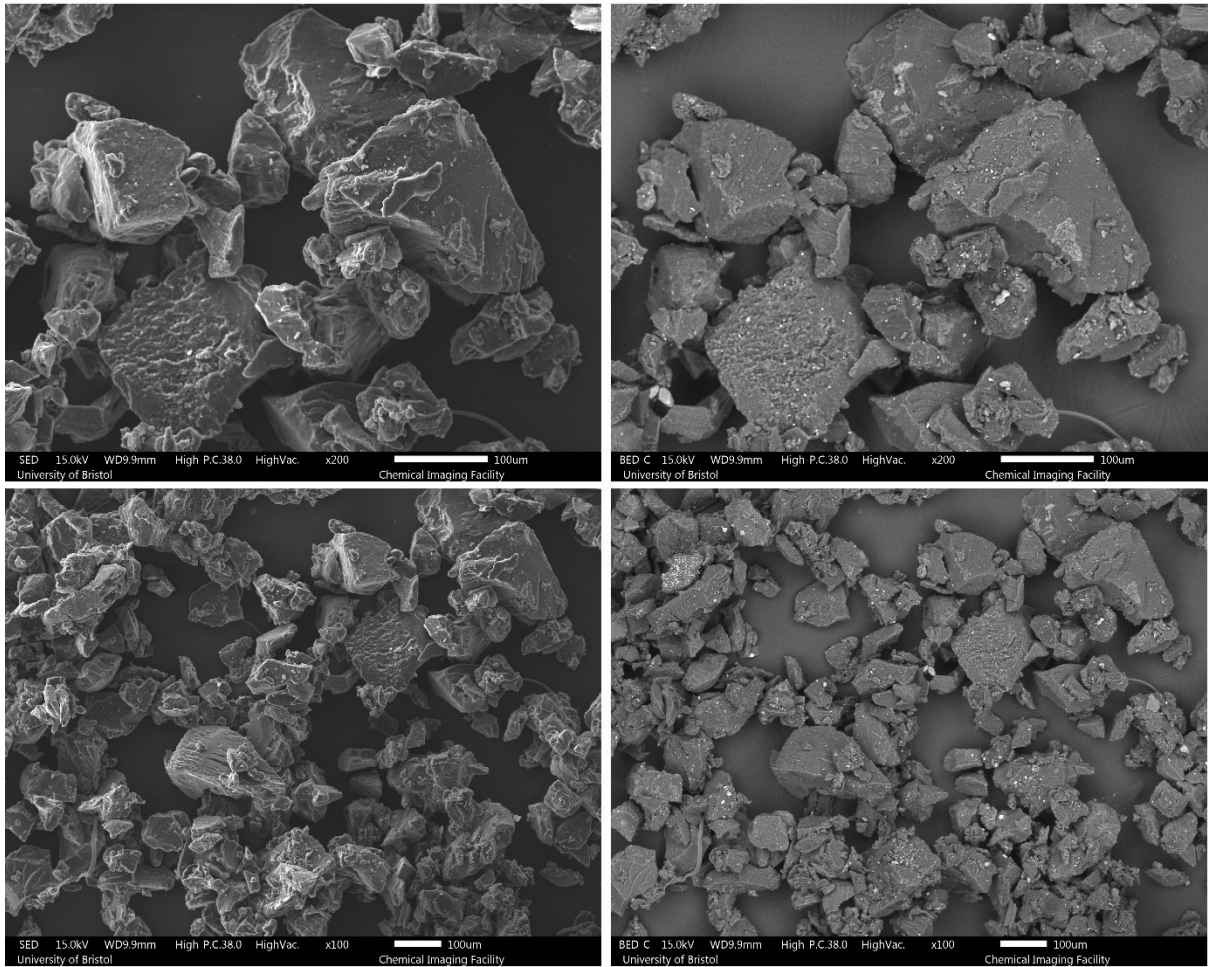
Figure 12. Different magnifications of 80 $M_{dv}$, left column: SED and right column: BED
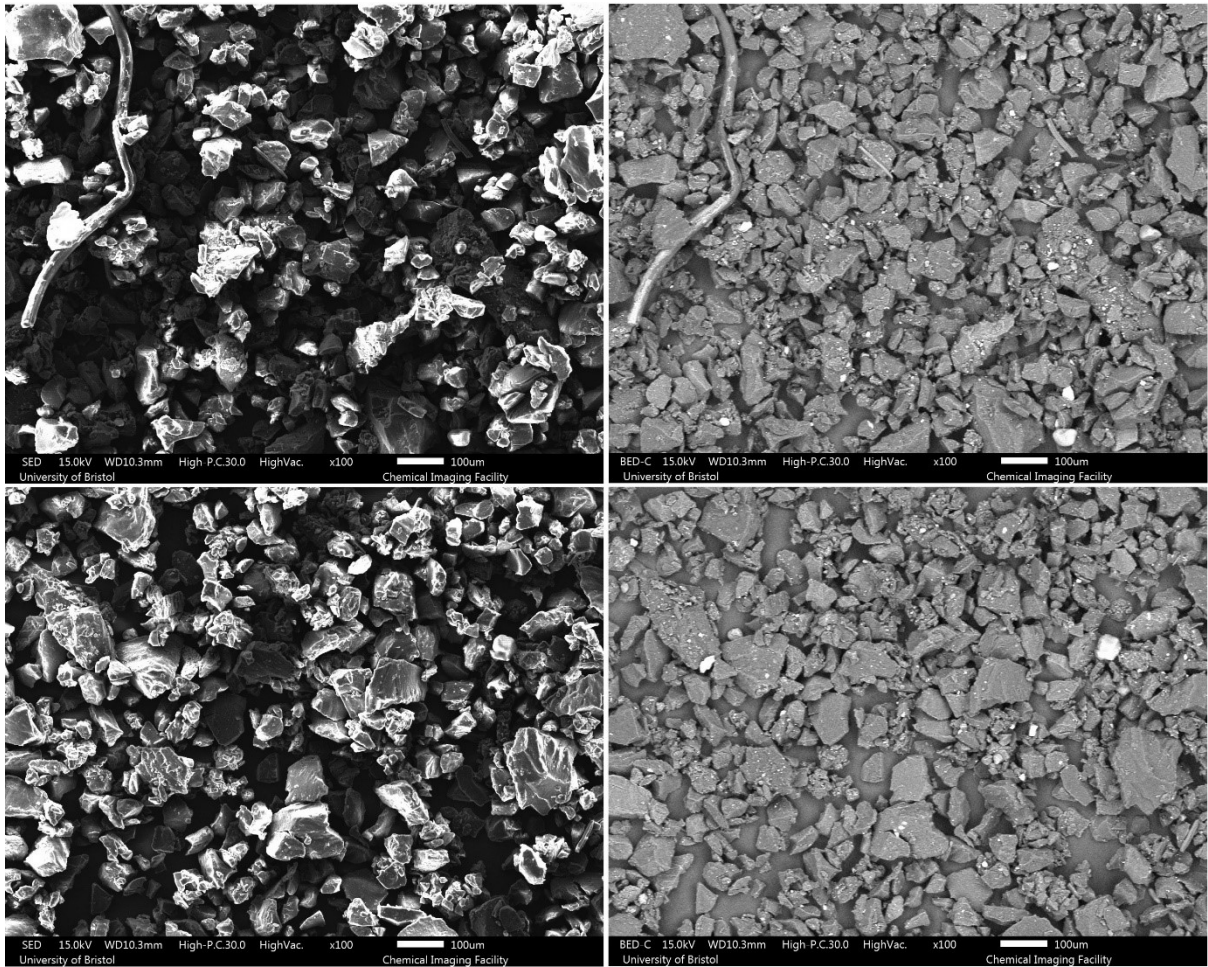
Figure 13. Different magnifications of 120 $M_u$, left column: SED and right column: BED
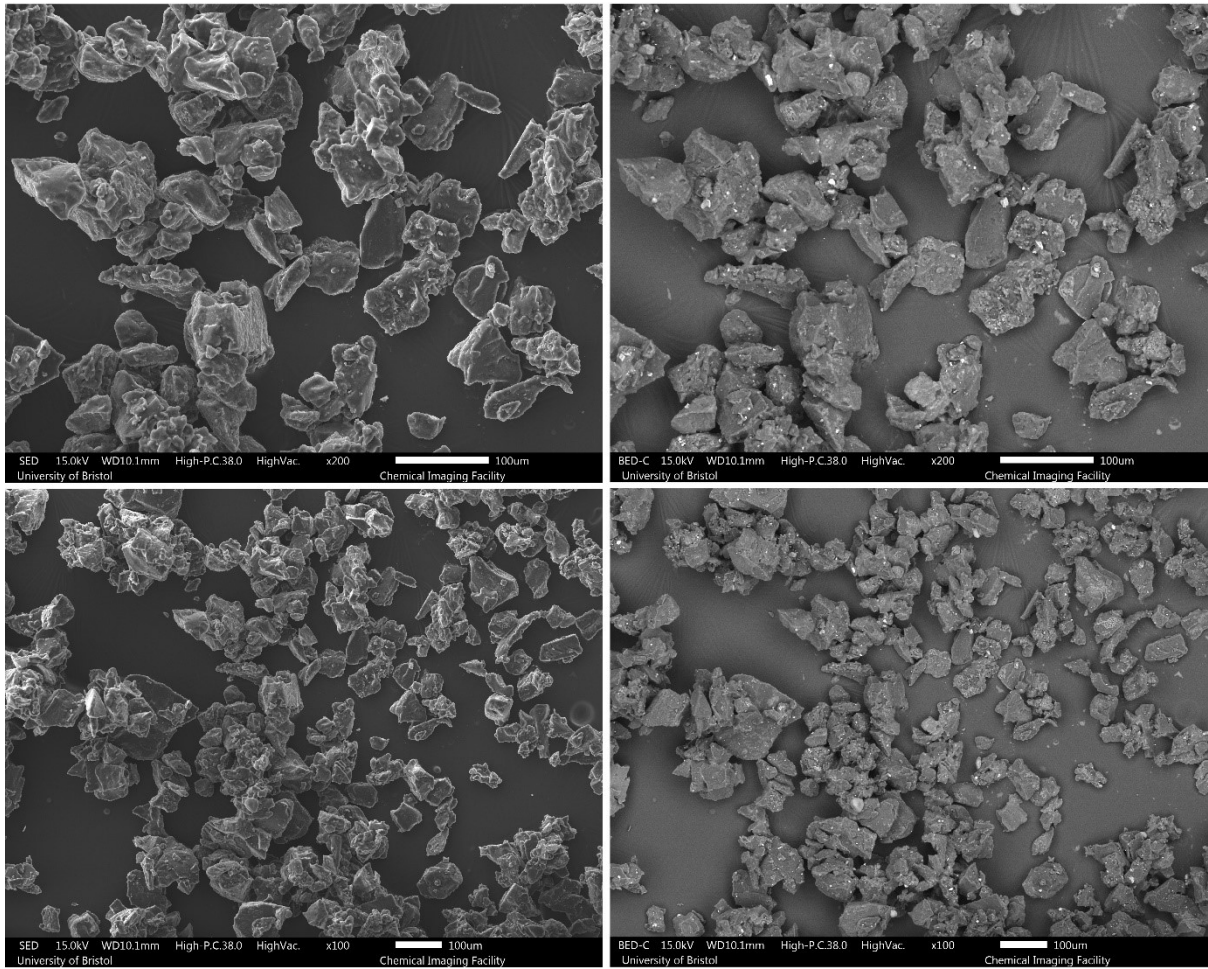
Figure 14. Different magnifications of 120 $M_{dv}$, left column: SED and right column: BED

# References

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