Electronic Supplementary Information for

Impact of calcium, zinc or aluminum dimethylphosphate coordination polymers on flame retardancy and rheological properties of poly(butylene succinate)

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Table S1. Thermogravimetric data of PBS and PBS/20%MtDOPs composites derived from TGA–FTIR tests carried out in nitrogen

Sample	Number of degradation steps[a]	T_{max}[b] (°C)	$T_{98\%}$[c] (°C)	$T_{95\%}$[c] (°C)	$T_{90\%}$[c] (°C)	$T_{50\%}$[c] (°C)	T_{end}[d] (°C)
PBS	1	424.59	369.02	386.87	397.34	420.90	457.34
PBS/20%CaDMP	multi	408.34	315.92	328.44	368.81	396.43	416.16
PBS/20%ZnDMP	2	419.35	320.04	354.51	381.14	413.79	435.59
PBS/20%AlDMP	2	383.14	340.20	351.00	362.12	381.29	394.67

[a] Refers to the number of steps in which thermal decomposition proceeded. [b] Temperature at the maximum decomposition rate. [c] T_x denotes the temperature, at which the sample mass reached x% of its initial value. [d] T_{end} denotes the temperature, at which the sample mass stabilized after thermal degradation.

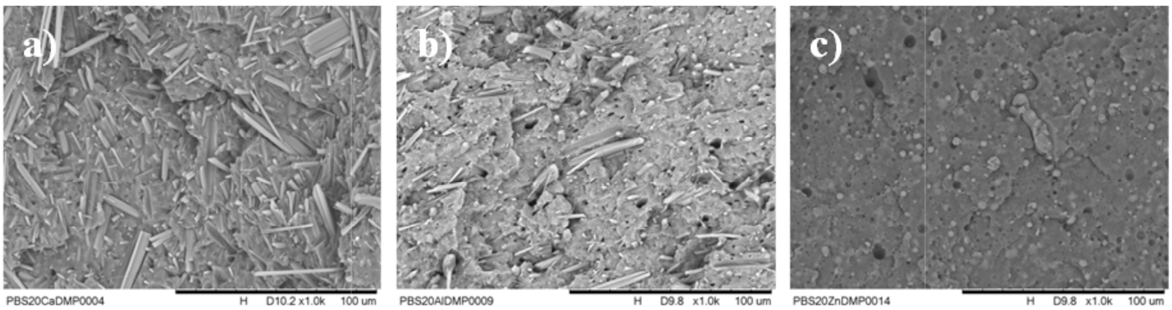

Fig. S1. SEM images of the cross-sections of the PBS composites filled with 20 wt.% of: a) CaDMP, b) AlDMP, c) ZnDMP obtained by means of injection moulding method. All images recorded at magnification of 1000×

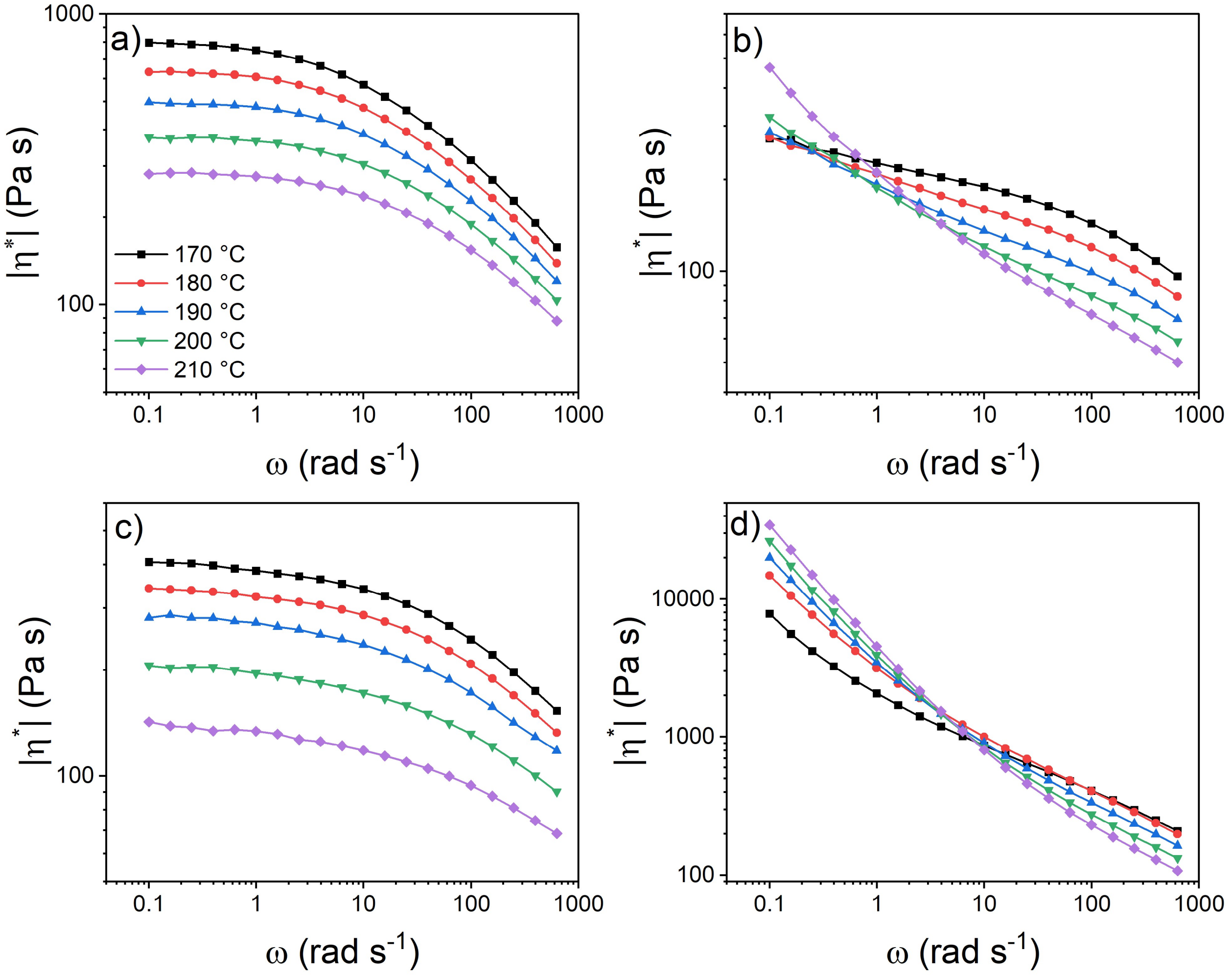

Fig. S2. Angular frequency dependence of complex viscosity recorded at different temperatures for: a) PBS, b) PBS/20%CaDMP, c) PBS/20%ZnDMP, and d) PBS/20%AlDMP

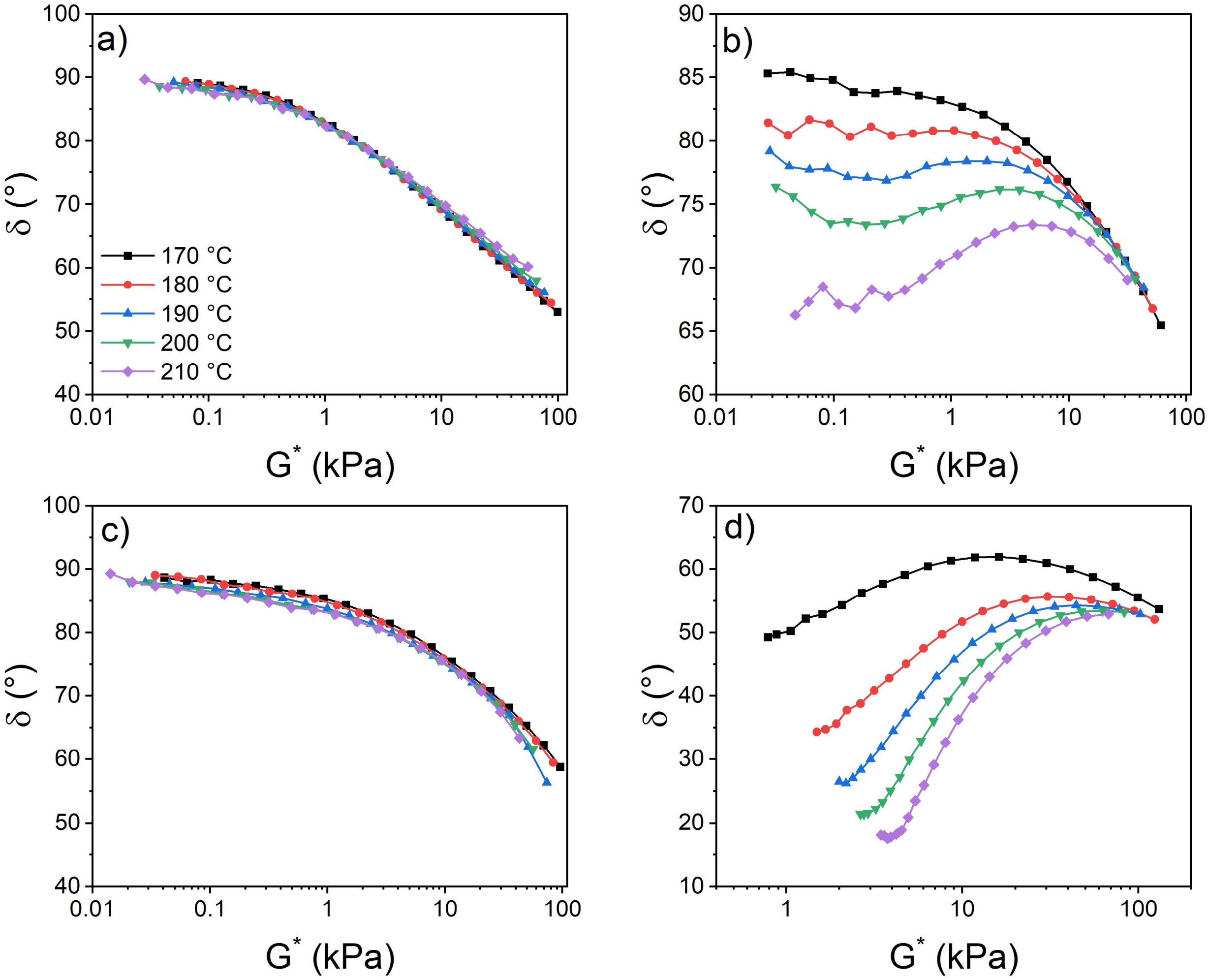

Fig. S3. Van Gurp–Palmen plots for: a) PBS, b) PBS/20%CaDMP, c) PBS/20%ZnDMP, and d) PBS/20%AlDMP

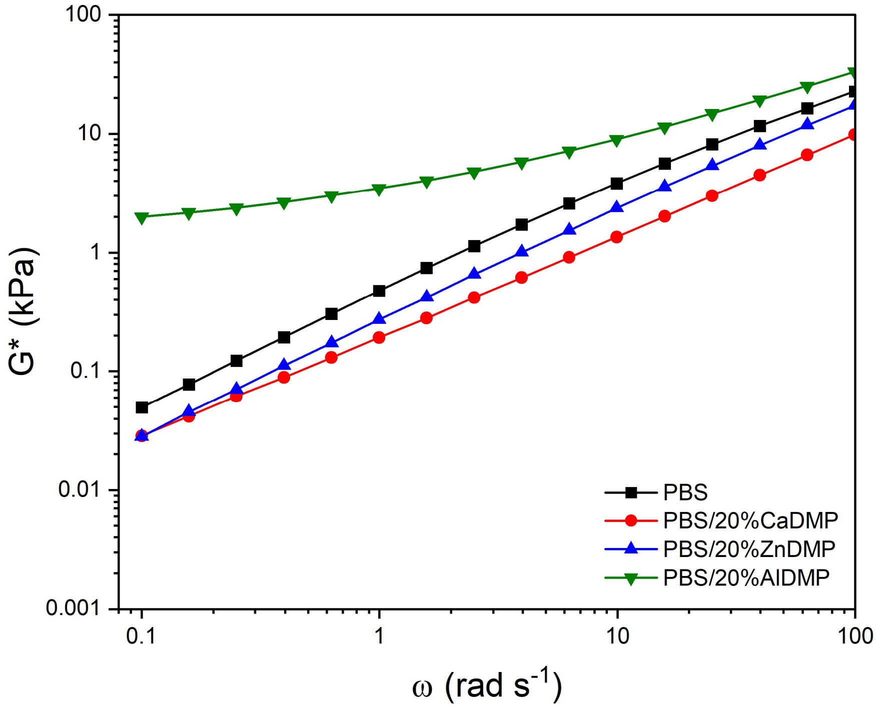

Fig. S4. Complex modulus variation in the low angular frequency region recorded at 190 °C

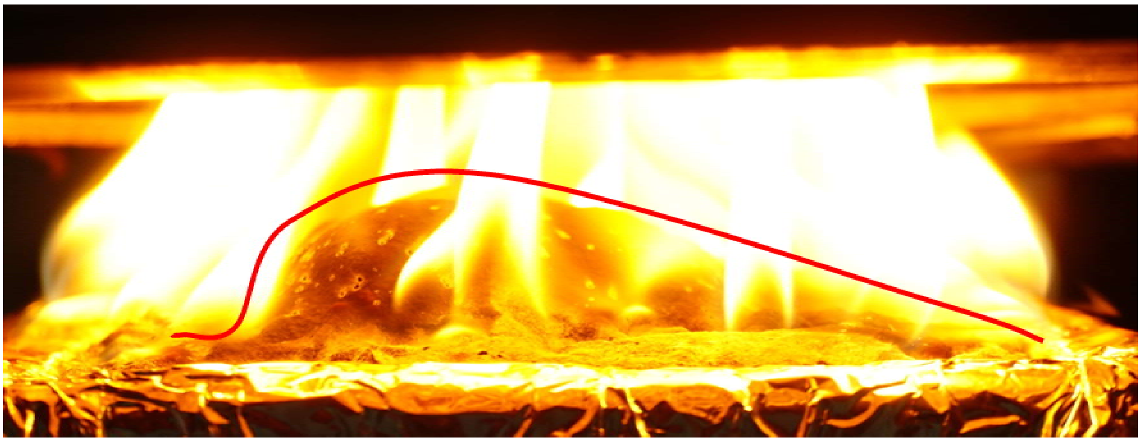

Fig. S5. Digital image of PBS/20%ZnDMP during burning in the MLC test

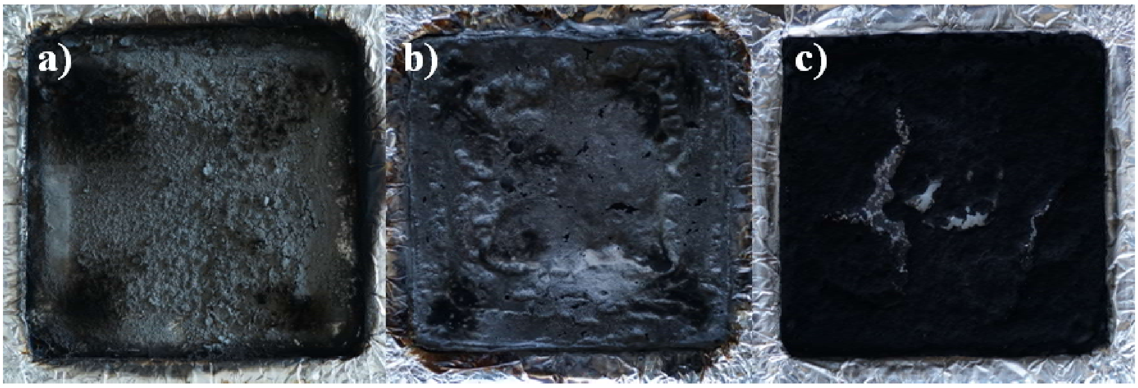

Fig. S6. Digital images of the surface of char residues obtained after the MLC tests for 20 wt.% composites of PBS with: a) CaDMP, b) ZnDMP, c) AlDMP

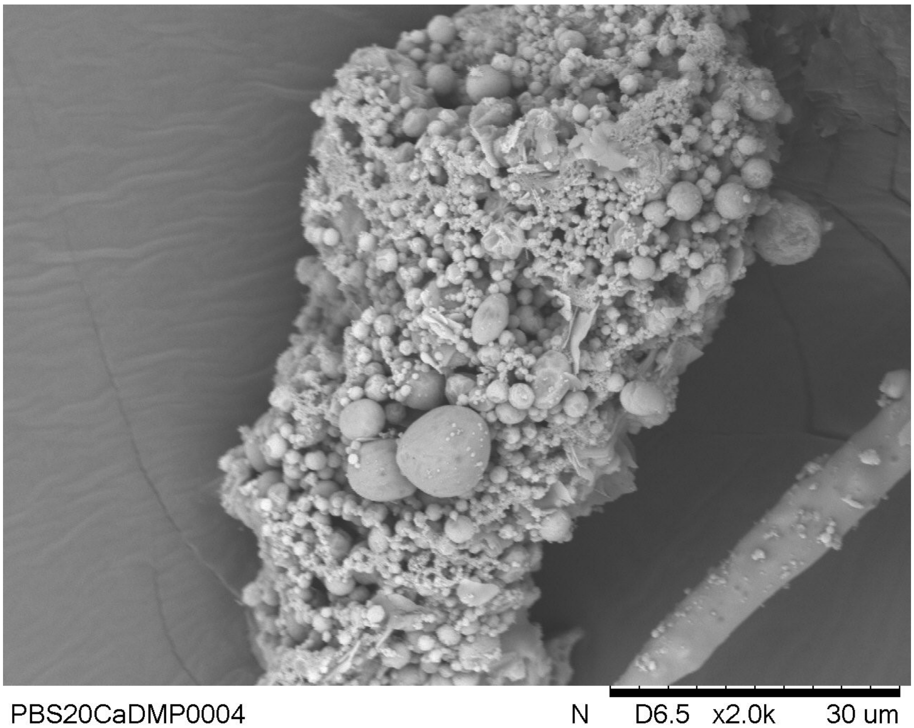

Fig. S7. SEM image of the internal structure of the solid residue obtained following the MLC test carried out for PBS/20%CaDMP. The image recorded at a magnification of 2000×

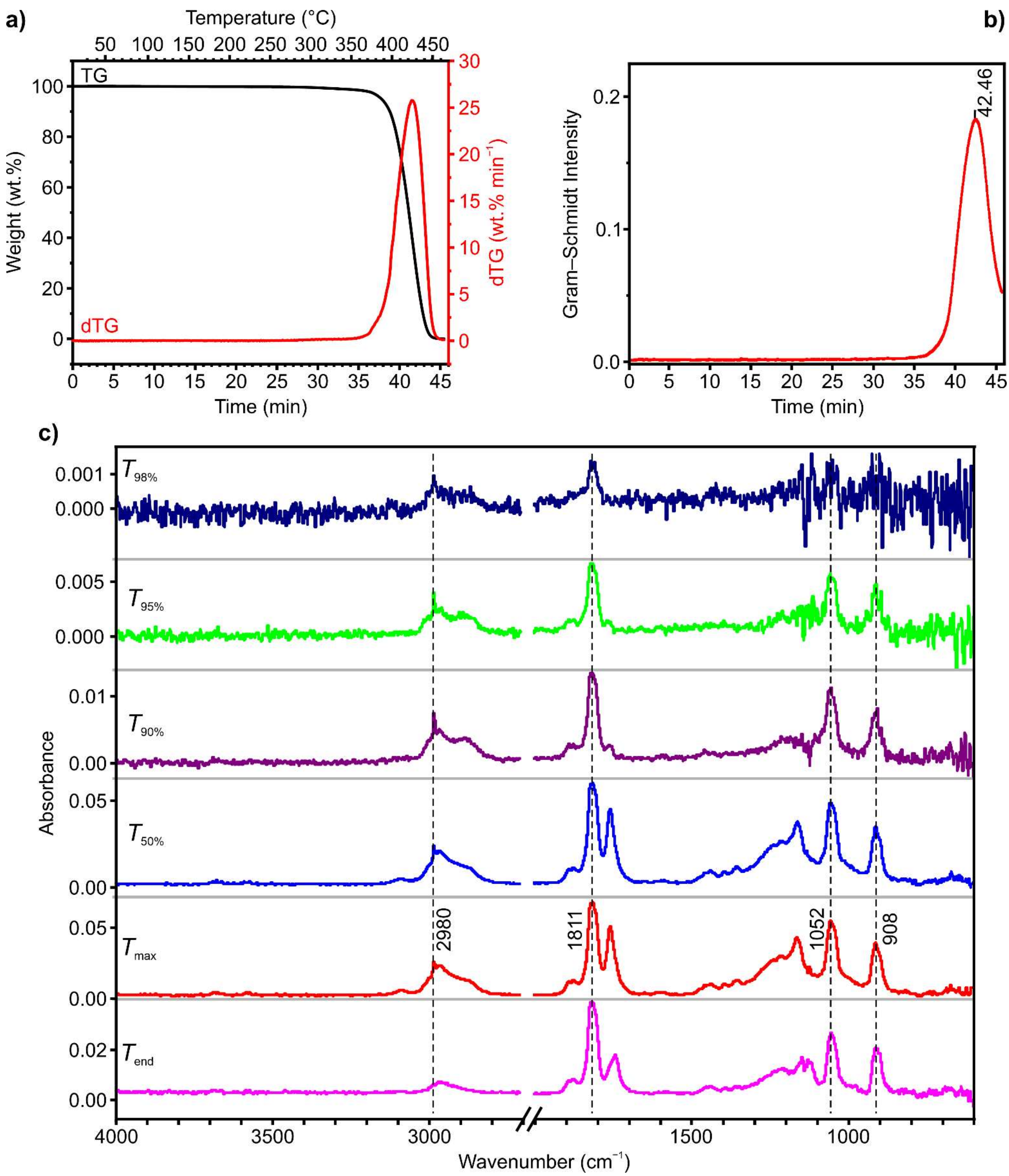

Fig. S8. TGA–FTIR analysis of PBS under nitrogen: a) mass loss (TG) and 1st derivative mass loss (dTG) curves, b) Gram-Schmidt curve, c) FTIR gas-phase spectra recorded at points associated with PBS characteristic temperatures as described in Table S1

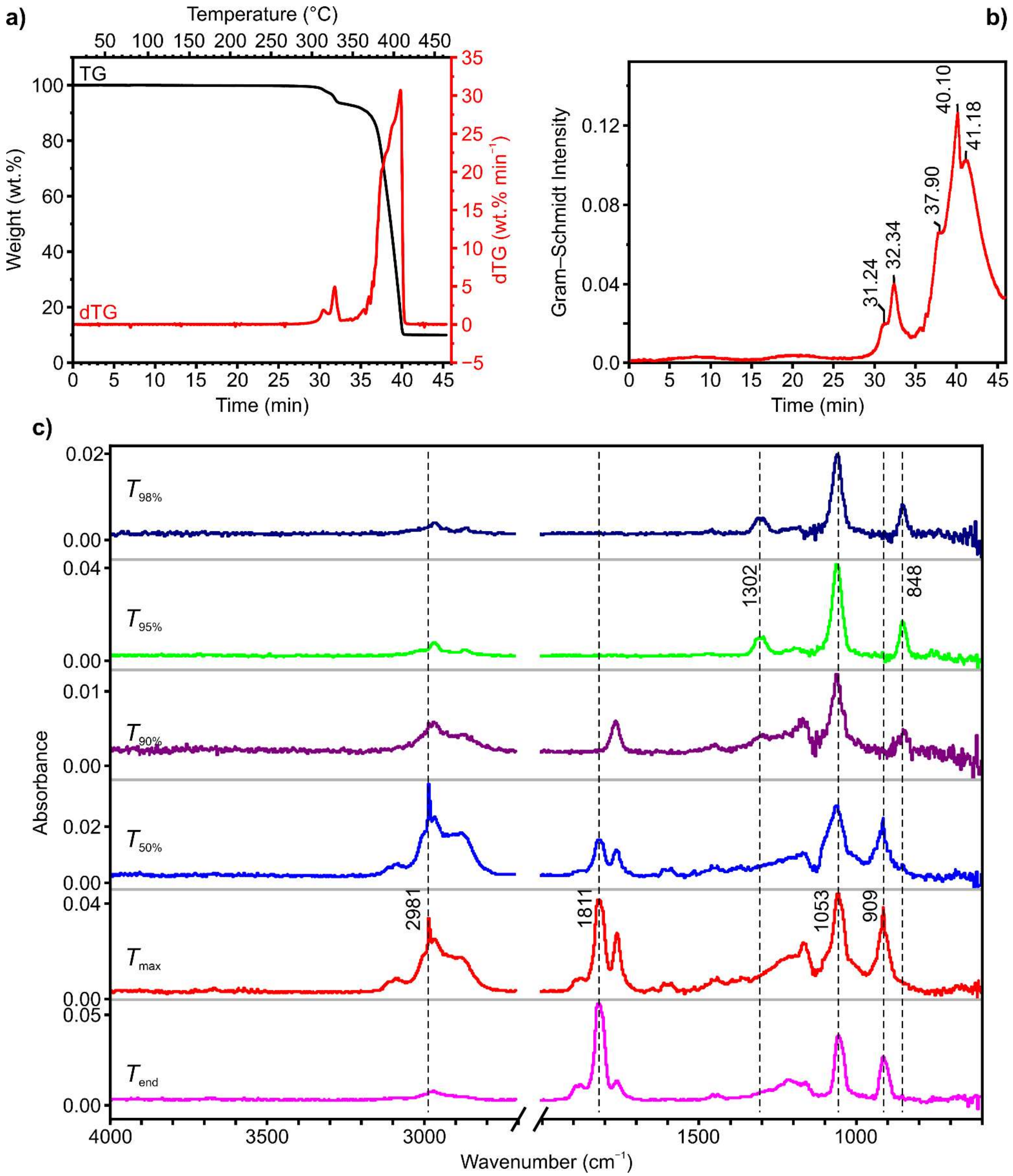

Fig. S9. TGA–FTIR analysis of PBS/20%CaDMP under nitrogen: a) mass loss (TG) and 1st derivative mass loss (dTG) curves, b)Gram-Schmidt curve, c) FTIR gas-phase spectra recorded at points associated with PBS/20%CaDMP characteristic temperatures as described in Table S1

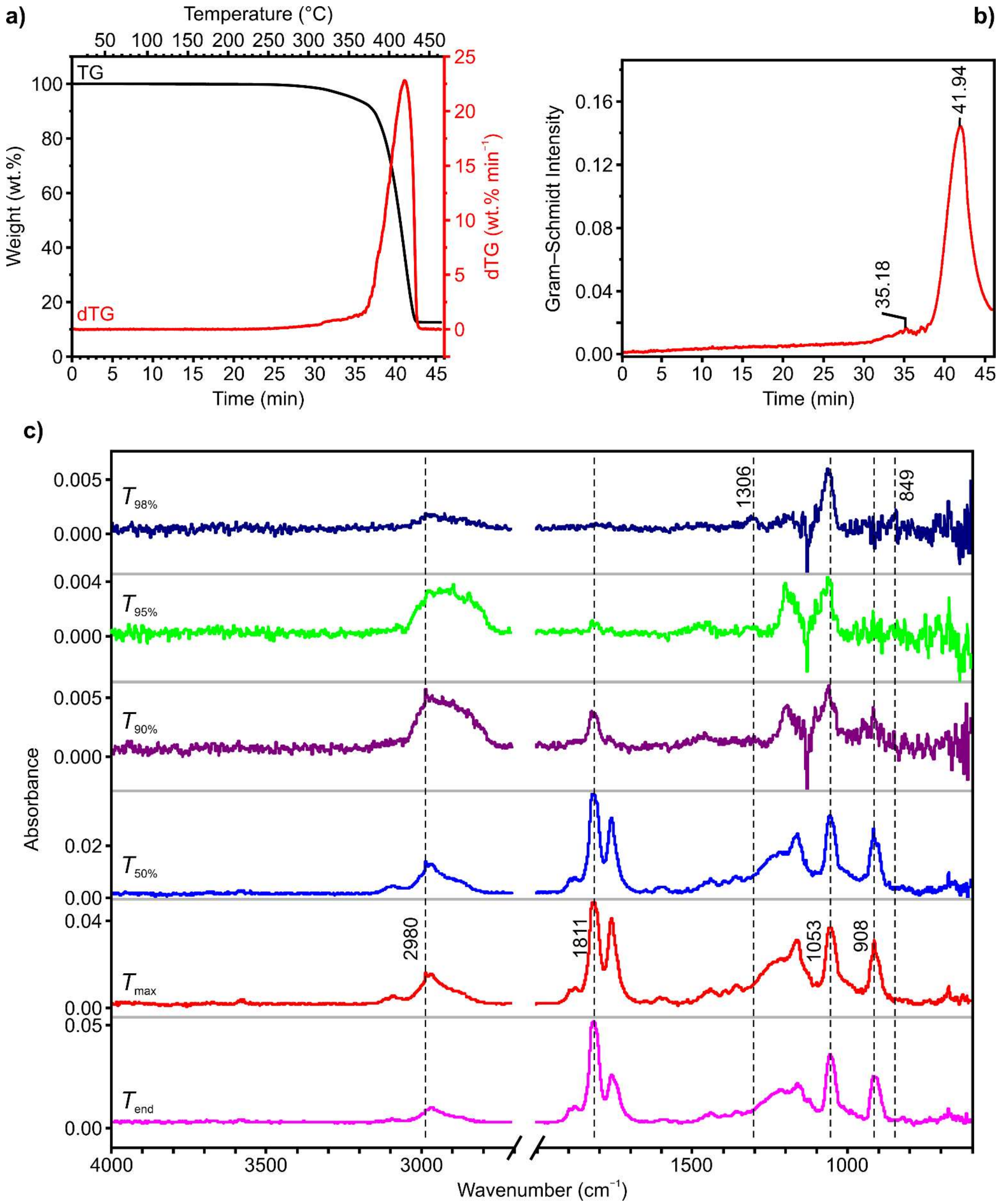

Fig. S10. TGA–FTIR analysis of PBS/20%ZnDMP under nitrogen: a) mass loss (TG) and 1st derivative mass loss (dTG) curves, b) Gram-Schmidt curve, c) FTIR gas-phase spectra recorded at points associated with PBS/20%ZnDMP characteristic temperatures as described in Table S1

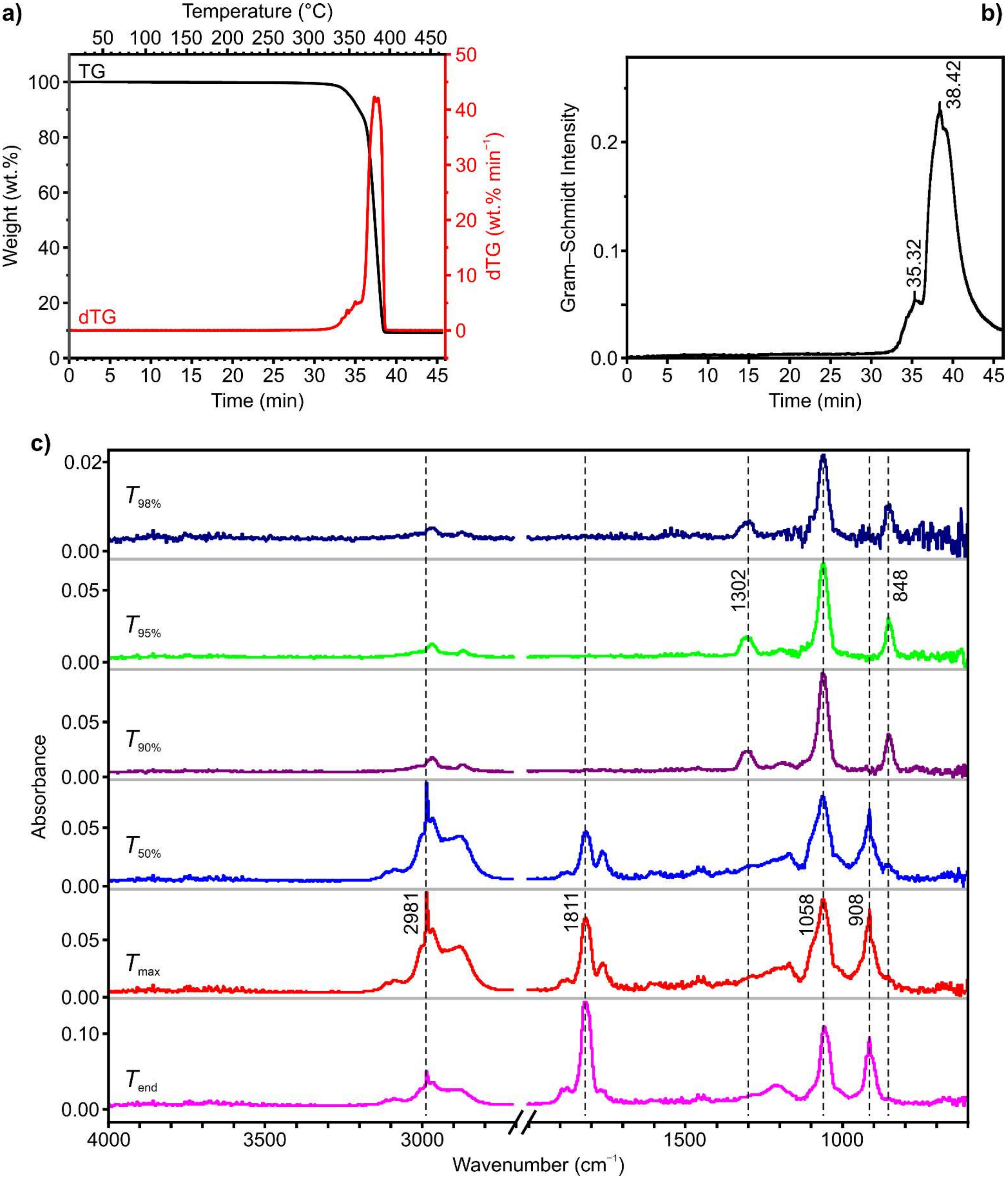

Fig. S11. TGA–FTIR analysis of PBS/20%AlDMP under nitrogen: a) mass loss (TG) and 1st derivative mass loss (dTG) curves, b) Gram-Schmidt curve, c) FTIR gas-phase spectra recorded at points associated with PBS/20%AlDMP characteristic temperatures as described in Table S1

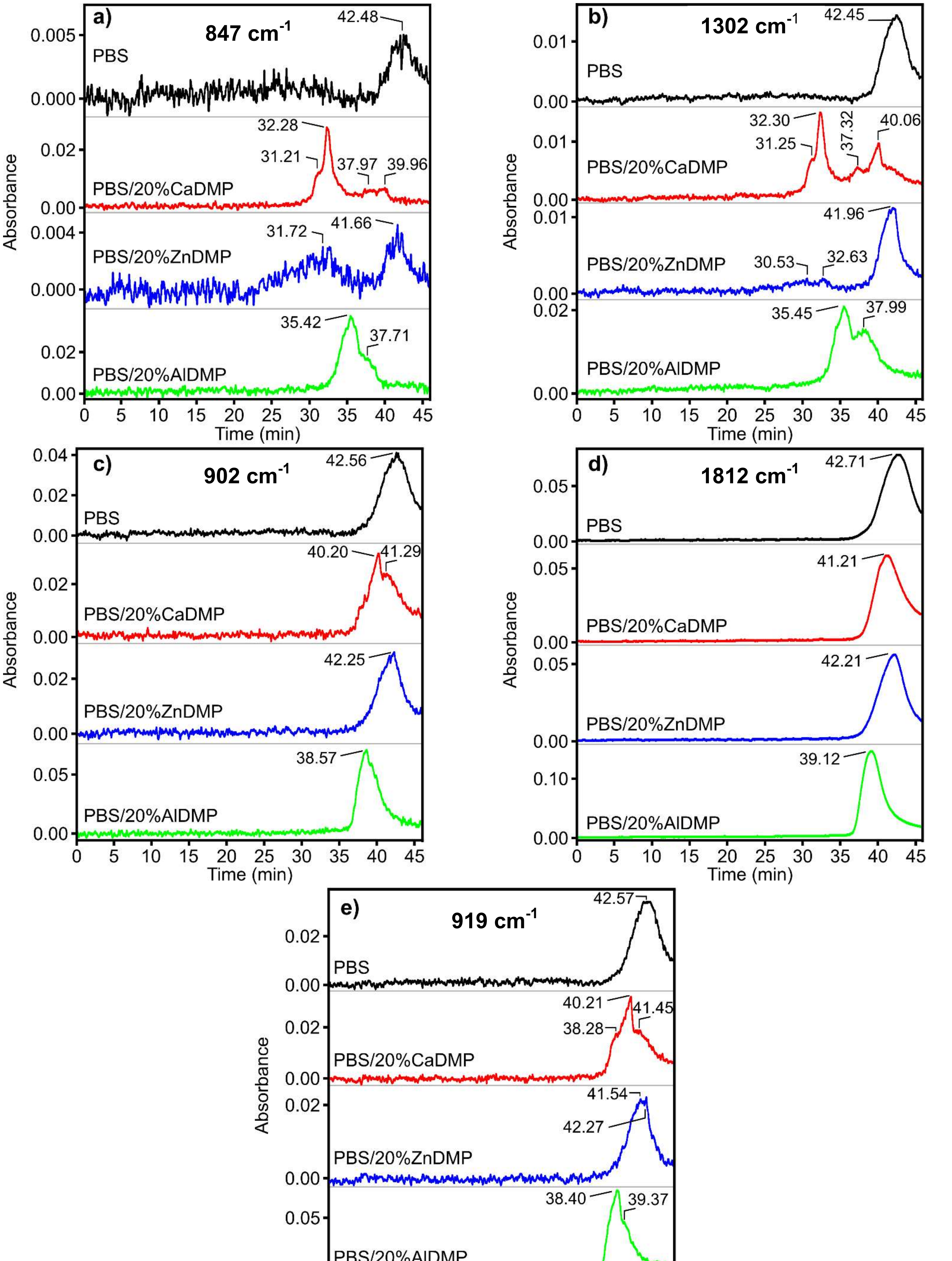

Fig. S12. Time profiles of the FT-FTIR diagnostic bands of TMP (a, b), succinic anhydride (c, d) and THF (e) obtained during EGA of PBS (black line) and its composites containing 20 wt.% of CaDMP (red line), ZnDMP (blue line) or AlDMP (green line)

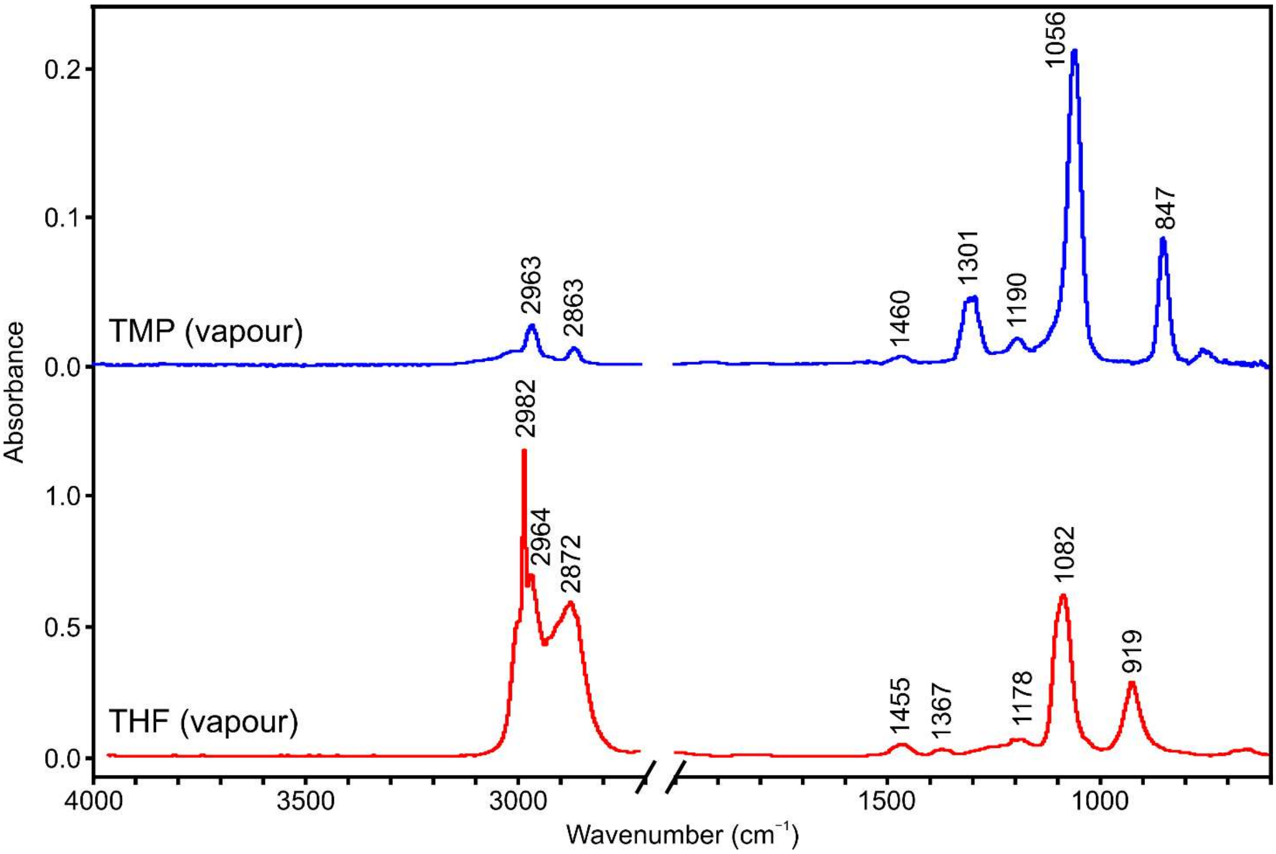

Fig. S13. Gas phase FTIR spectra of: a) TMP reference sample heated at 126.80 °C, and b) THF obtained from the NIST spectral database [NIST Standard Reference Database 69: *NIST Chemistry WebBook.* https://webbook.nist.gov/cgi/cbook.cgi?ID=C109999&Units=SI&Type=IR-SPEC&Index=0#IR-SPEC, accessed 15 December] 2025)

$$FI = \left(1 - \frac{avEHC_{composite}}{avEHC_{polymer}}\right) \times 100\% \quad \text{(S1)}$$

$$Ch = \left(\frac{CY_{composite} - CY_{polymer}}{100\% - CY_{polymer}}\right) \times 100\% \qquad \text{(S2)}$$

$$BaPL = \left(1 - \frac{pHRR_{composite} \times pHRR_{polymer}^{-1}}{THE_{composite} \times TH\ _{polymer}^{-1}}\right) \times 100\% \quad \text{(S3)}$$

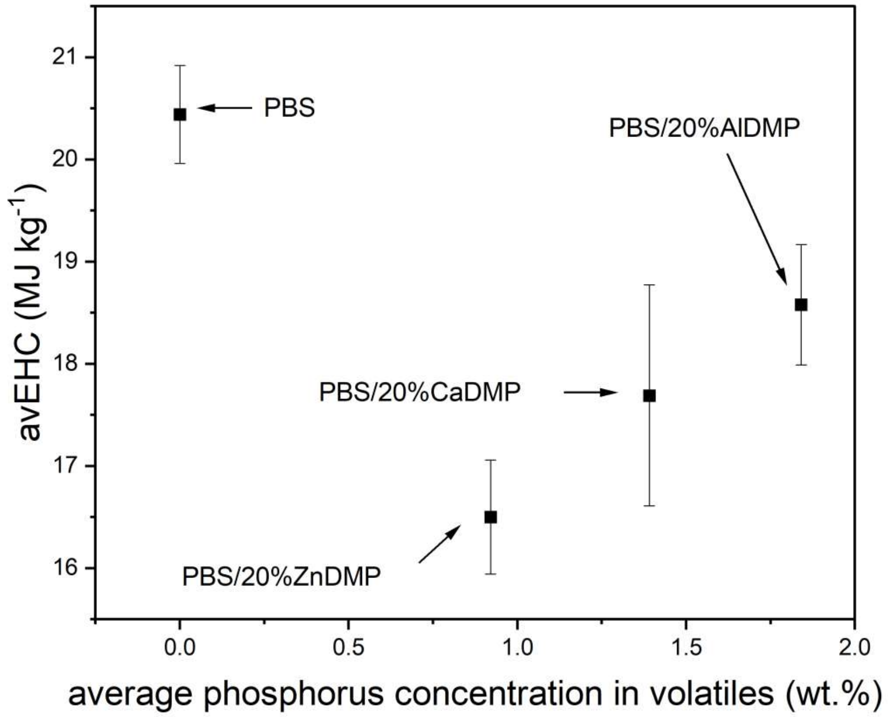

Fig. S14. avEHC dependency of the average phosphorus concentration in volatiles

Derivation of an equation governing the mean phosphorus concentration in volatile compounds

The average phosphorus concentration in the volatiles is given by the Equation 4.

$$c_P = \frac{m_P}{m_V} \times 100\% \text{ (S4)}$$

m_P can be calculated as a difference between the mass of phosphorus in the sample of the composite before combustion and mass of phosphorus in the char residue.

$$m_P = m_{P(s)} - m_{P(Ch)} \text{ (S5)}$$

$m_{P(s)}$ and $m_{P(Ch)}$ are given by Equations (6) and (7) respectively:

$$m_{P(s)} = m_{Mt(s)} \times f_s \text{ (S6)}$$
$$m_{P(Ch)} = m_{Mt(Ch)} \times f_{Ch} \text{ (S7)}$$

Assuming no emissions of volatile compounds of calcium or zinc or aluminum during combustion of PBS/20%MtDOPs:

$$m_{Mt(Ch)} = m_{Mt(s)} = 20\% \times c_{Mt} \times m_s \text{ (S8)}$$

By combining Eq. 5 – 8 we obtain:

$$m_P = 20\% \times c_{Mt} \times m_s \times (f_s - f_{Ch}) \text{ (S9)}$$

m_V is correlated with *CY* by following equation:

$$m_V = m_s \times \left(1 - \frac{CY}{100\%}\right) \text{ (S10)}$$

By combining Eq. 4, 8 and 9, we obtain:

$$c_P = \frac{20\% \times c_{Mt} \times (f_S - f_{Ch})}{100\% - CY} \times 100\% \text{ (S11)}$$

where c_P - average phosphorus concentration in the volatiles, c_{Mt} – weight fraction of Ca or Zn or Al in corresponding MtDOP, f_s – measured by EDS weight P/Mt weight ratio in corresponding MtDOP, f_s – measured by EDS weight P/Mt weight ratio in corresponding MtDOP, f_{Ch} – measured by EDS weight P/Mt weight ratio in corresponding char residue, m_P – mass of phosphorus released to the gas phase during combustion of corresponding composite, $m_{P(s)}$ – mass of the phosphorus in sample of corresponding composite before combustion, $m_{P(Ch)}$ – mass of the phosphorus in char residue after combustion of corresponding composite, m_V – total mass of the volatiles released during combustion of the corresponding composite, m_s – mass of the sample of composite subjected MLC test, $m_{Mt(s)}$ – mass of Ca or Zn or Al in the sample of corresponding composite before combustion, $m_{Mt(Ch)}$ – mass of Ca or Zn or Al in char residue after combustion of the corresponding composite, CY – char yield after combustion of the corresponding composite