Development of a mechanistic kinetic model for the thermal pyrolysis of plastic from WEEE

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INTRODUCTION

The quantity of waste of electric and electronic equipment (WEEE) in Europe amounts to 9.5 million tonnes per year, of which 1.2 million tonnes are plastic materials, composed in majority by polystyrene (PS) and acrylonitrile-butadiene-styrene (ABS).[1] Mechanical recycling of plastic from WEEE faces difficulties due to the complicated sorting processes required to achieve pure polymer streams.[1] Chemical recycling is an alternative to treat this kind of waste since it provides a way to convert the waste plastic, even when it is composed of mixed components, into valuable products for the chemical industry.[2] The aim of this work is to investigate the thermal pyrolysis of PS and ABS from WEEE under dynamic and isothermal conditions by thermogravimetric analysis coupled with differential scanning calorimetry (TG/DSC). The co-pyrolysis of these two plastics is also studied for mixtures of 80/20, 60/40, 50/50, 40/60 and 20/80. A mechanistic kinetic model capable of describing the experimental TG/DTG data is developed.

EXPERIMENTAL SETUP

Materials

Waste ABS from food blender
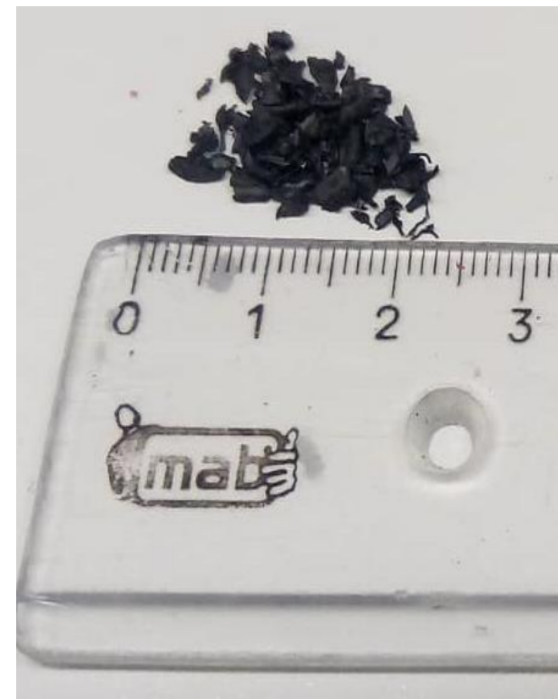
Waste PS from TV outer casing

Method

TG Analysis - Equipment: Perkin-Elmer STA 6000 simultaneous thermal analyser.

❑ **Individual polymer analysis**
- **Dynamic conditions:** 40 - 900 °C; 10 °C/min; N_2 flow of 20 mL/min.
- **Isothermal conditions:** t=90 min, 40 °C until T=400, 420, 440, 500 °C, 10 °C/min, N_2 flow of 20 mL/min.

❑ **Mixture Analysis**
- Mixtures of: 80/20, 60/40, 50/50, 40/60, 20/80.
- 40 - 900 °C, Heating rate=10 °C/min, N_2 flow of 20 mL/min.

KINETIC MODEL

❑ Model development based on the generic reaction rate (Eq. 1). Bootstrapping tool for estimation of kinetic parameter deviation.

❑ **Individual polymer degradation**
- Overall fitting to the experimental data at dynamic conditions, from which a single set of kinetic parameters was obtained.
- Model validation: estimated kinetic parameters applied to the data from the isothermal conditions.
- For both waste PS and ABS, the model considers the degradation of two pseudo-component decompositions in parallel (Eq. 2). The pseudo-components are independent of each other and first-order kinetics is considered.

❑ **Mixtures**
- Overall fitting to the different plastic mixture compositions, from which a single set of kinetic parameters was obtained (Eq.3).

$$\frac{dW_{j,i}}{dt} = -k_{ref\,j,i}e^{-\frac{E_{a\,j,i}}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)}W_{j,i} \quad \text{(Eq. 1)}$$

$$j = PS, ABS;\ i = component\ 1,2$$

$$\frac{dW_j}{dt} = \sum_{i=1}^{2}\frac{dW_{j,i}}{dt} \quad \text{(Eq. 2)}$$

$$\frac{dW_{Mixture}}{dt} = x\frac{dW_{PS}}{dt} + (1-x)\frac{dW_{ABS}}{dt} \quad \text{(Eq. 3)}$$

RESULTS

TGA results

- PS degradation starts at a lower temperature than ABS (355 °C and 384 °C, respectively).
- 1st degradation peak of waste PS → presence of an additive (Fig. 1).
- Mixing PS with ABS reduces onset temperature (<355 °C) → ABS might accelerate the degradation of the additive present in waste PS (Fig. 2) showing that interactions between the two materials occur.
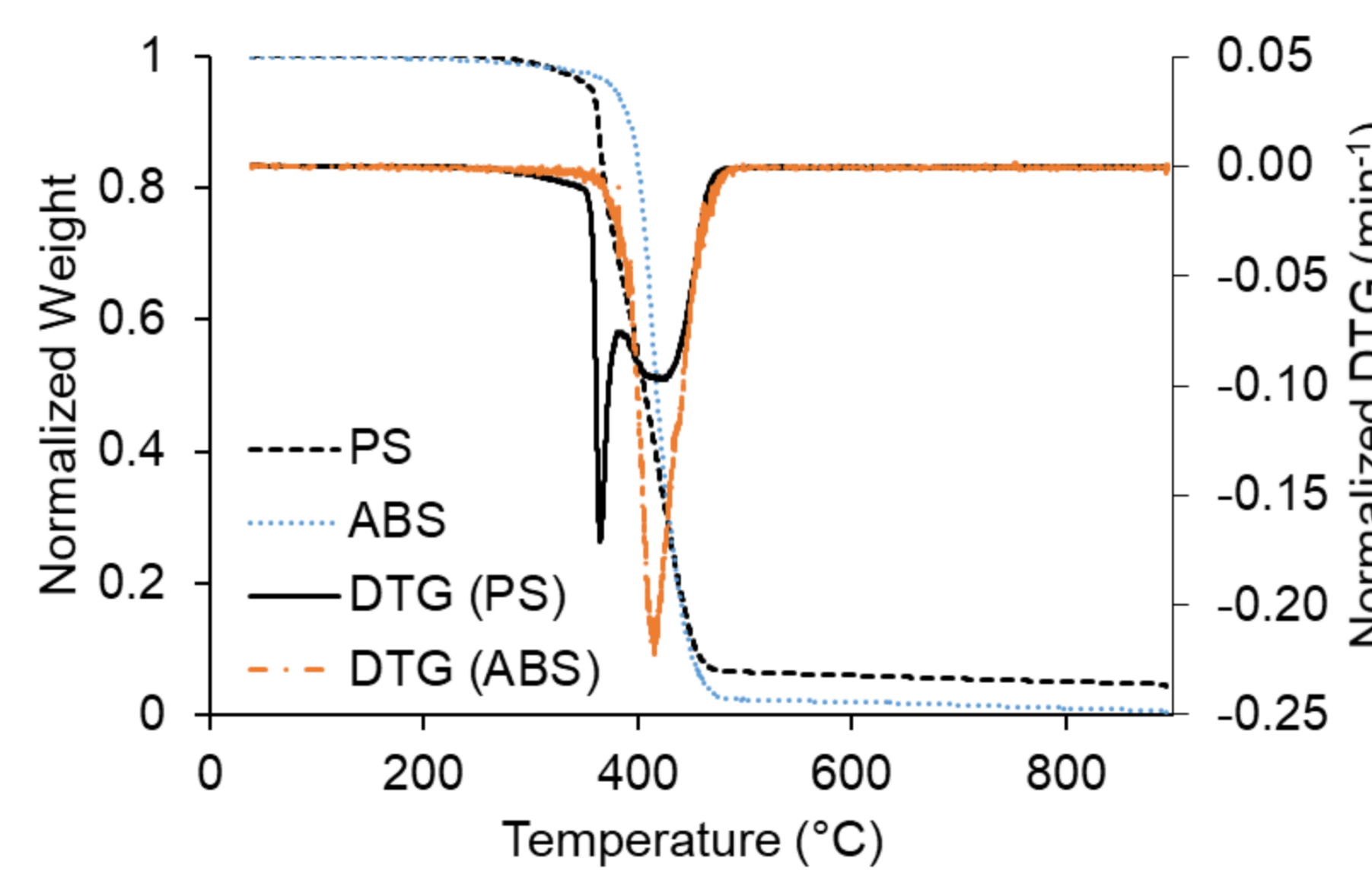

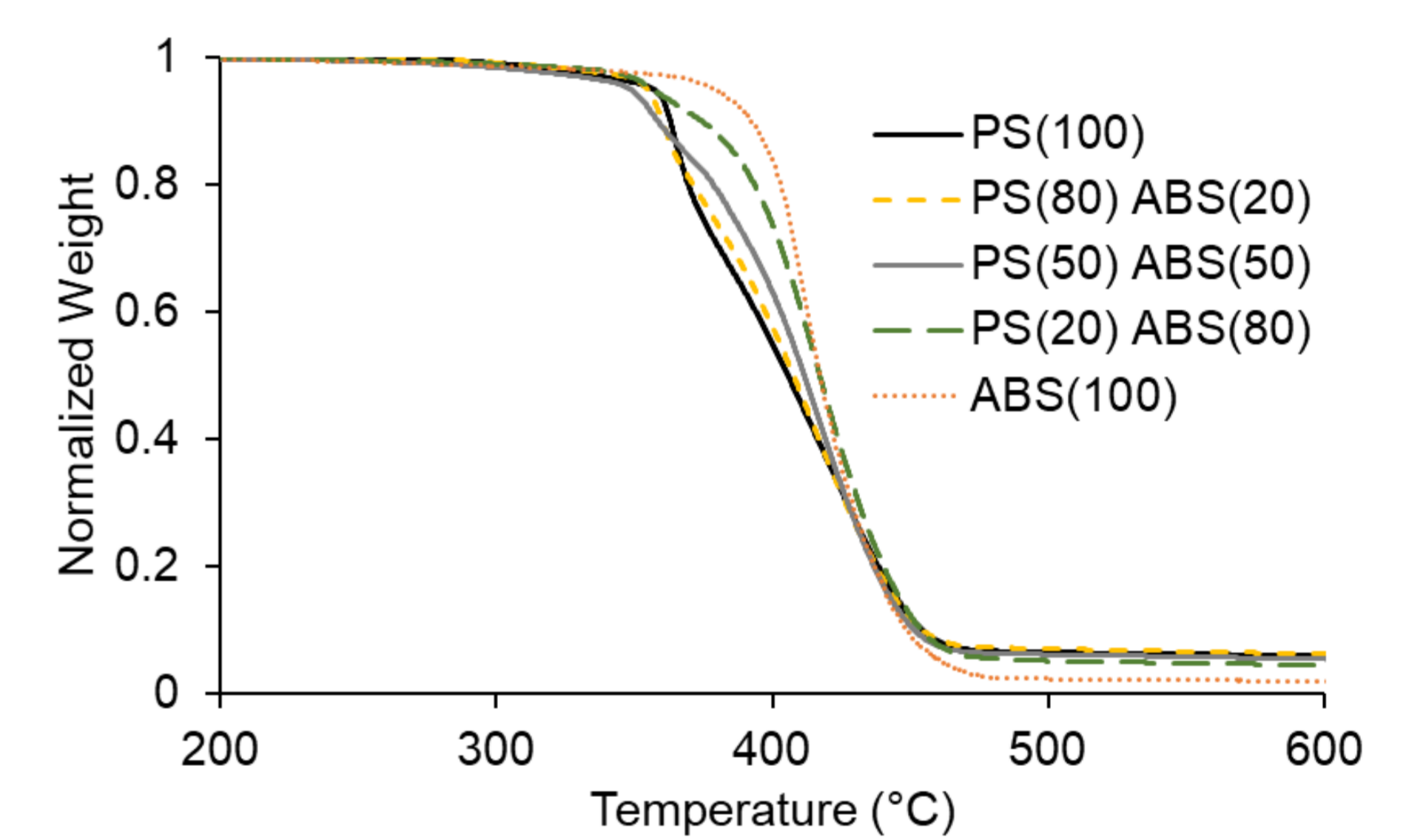
Fig. 1 – TG/DTG results for waste PS and ABS.

Fig. 2 – TG results for mixtures of waste PS/ABS.
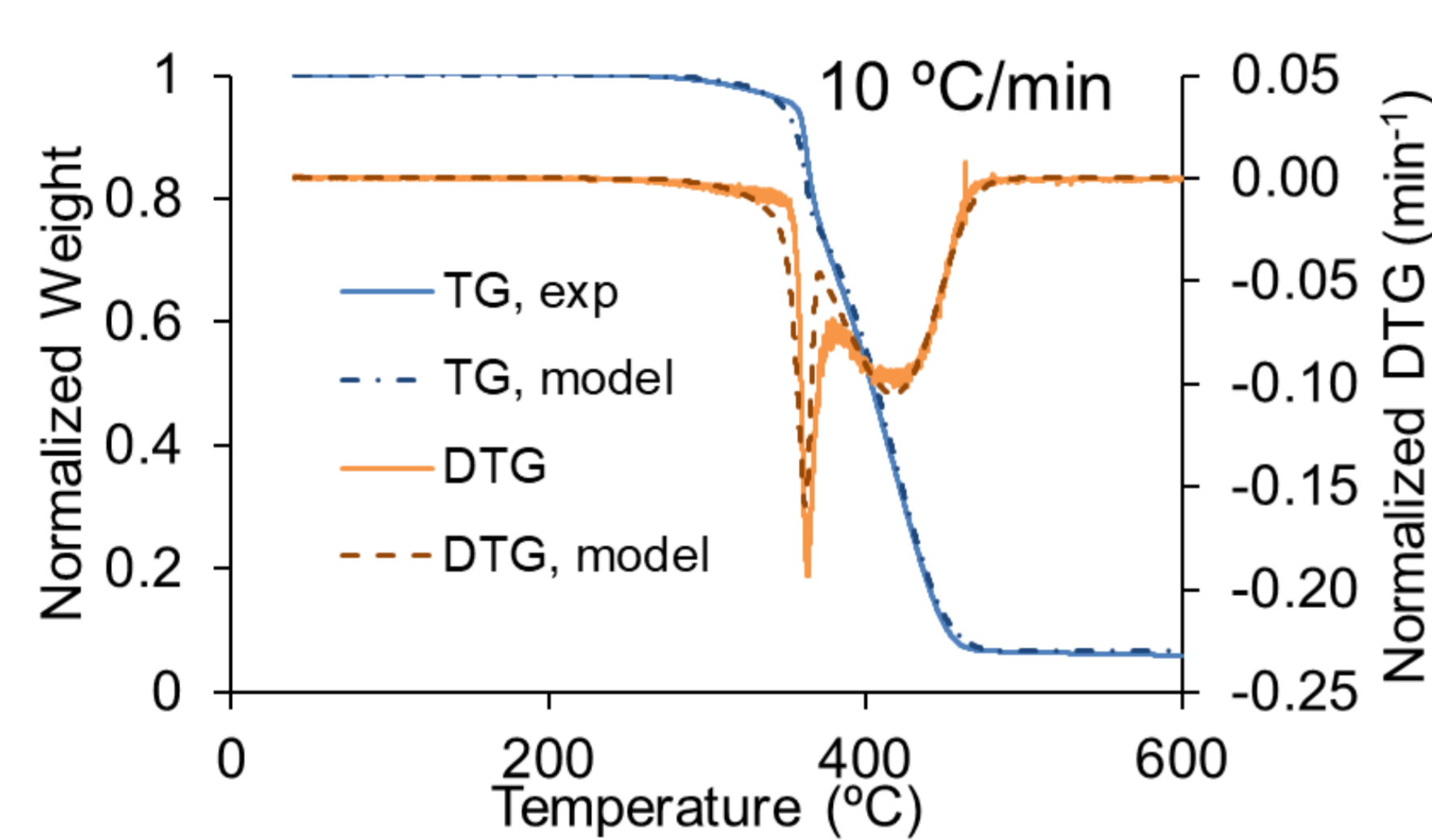
Kinetic model

Fig. 3 – Model and experimental data for waste PS.
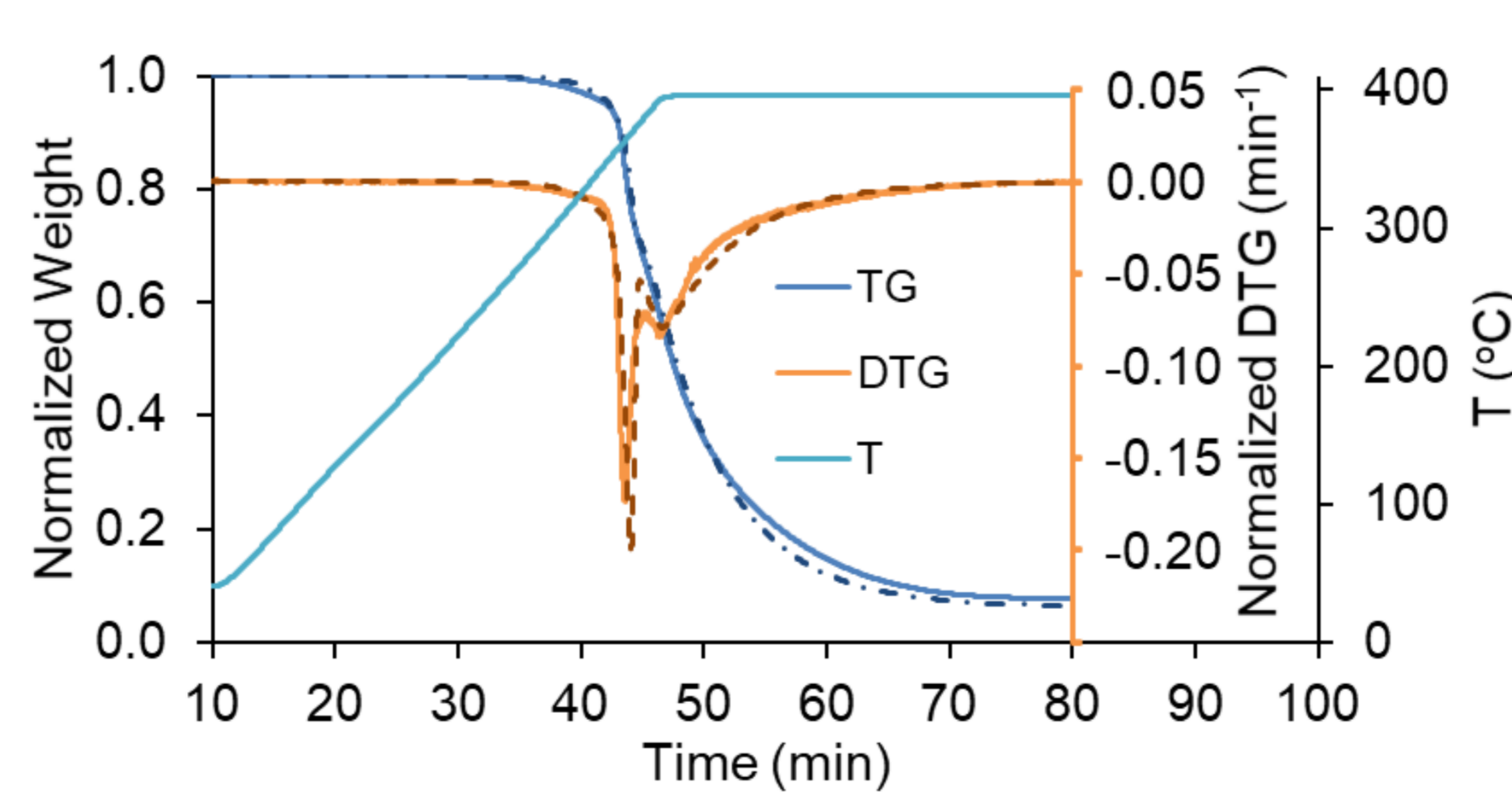

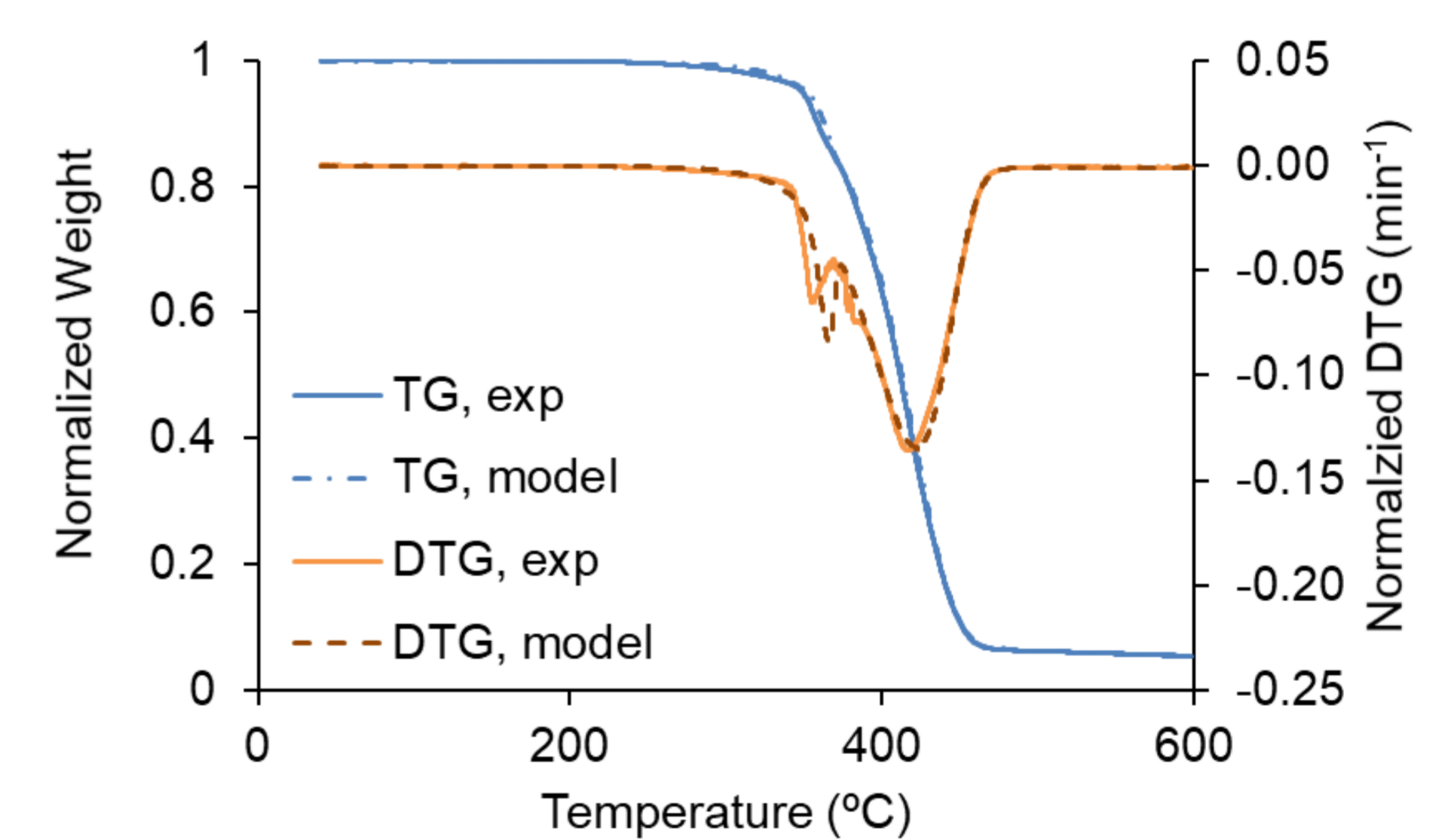Fig. 4 – Model validation for waste PS (isothermal).

Fig. 5 – Model and experimental data for 50/50 mixture.

Tab. 1 – Estimated kinetic parameters for waste PS, ABS and mixtures.

Parameter	PS	ABS	Mixtures
$E_{a,1,\,PS}$ (kJ/mol)	815 ± 2		761 ± 11
$k_{ref,1,\,PS}$ (1/s)	284 ± 14		65 ± 8
$E_{a,2,\,PS}$ (kJ/mol)	128 ± 1		123.8 ± 0.1
$k_{ref,2,\,PS}$ (1/s)	(296 ± 3) x 10^{-5}		4 x 10^{-3} ± 2 x 10^{-6}
$E_{a,1,\,ABS}$ (kJ/mol)		255 ± 3	189.0 ± 0.2
$k_{ref,1,ABS}$ (1/s)		(32 ± 1) x 10^{-4}	2 x 10^{-3} ± 2 x 10^{-6}
$E_{a,2,\,ABS}$ (kJ/mol)		193 ± 5	28.2 ± 0.1
$k_{ref,2,\,ABS}$ (1/s)		(11 ± 1) x 10^{-4}	6 x 10^{-4} ± 3 x 10^{-6}

- Model describes the individual degradation of waste plastic at dynamic and isothermal conditions (Fig. 3 and 4) → model is validated.
- Model can be applied to mixtures even with the presence of interactions between polymers (Fig. 5).
- The 1st Ea related to the 1st peak of degradation of waste PS decreases in the presence of ABS from 815 to 761 kJ/mol → mixture facilitates the degradation of the possible additive. Some chemical interactions between the PS additive and ABS might occur.

CONCLUSIONS

- Interactions between both polymers, PS and ABS, seem to occur for different mixtures compositions.
- The activation energies of the plastics in the mixtures are lower than of the single plastics, which is relevant for the development of a pyrolysis process.
- Developed mechanistic model describes the thermal degradation of different plastics from WEEE under dynamic and isothermal conditions with a single set of kinetic parameters as well as the co-pyrolysis of WEEE mixtures.

REFERENCES

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2. Buekens A., Introduction to Feedstock Recycling of Plastics, In: Feedstock Recycling and Pyrolysis of Waste Plastics, Scheirs J., Kaminsky W., John Wiley & Sons, Ltd., Chichester, 2006, pp. 3-42.

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