

Theses

Determination of Ageing with the Essential Work of Fracture Method in Thermoplastic Polyesters

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Thesis 1 The method of essential work of fracture (DEN-T specimen) can be applied in the characterization of the physical ageing of polyesters (PET, PETG) in thermal and damp conditions.

- a. The following linear relationship was found between specific yielding-related essential work of fracture ($w_{e,y}$) and yield stress (σ_y):

$$w_{e,y} = a \cdot \sigma_y + b$$

The relation was verified for both PETG and PET, independently, where $a=0.00045$ m for both materials, while $b= -11.3$ kJ/m² in case of PETG, and $b= -9.7$ kJ/m² for PET.

- b. The following linear relation is valid between specific yielding-related essential work of fracture ($w_{e,y}$) and enthalpy relaxation (ΔH) in case of dry ageing:

$$w_{e,y} = a \cdot \Delta H + b,$$

where a and b are 890 g/m² and 11 kJ/m², respectively in case of PETG and 410 g/m² and 13 kJ/m² in case of PET.

- c. The crack propagation component of specific plastic work of fracture ($\beta''w_{p,n}$) can be applied to trace physical ageing in case of dry ageing of the examined polyesters (PETG, PET). $\beta''w_{p,n}$ and yield stress, as well as enthalpy relaxation are in indirect proportion. A good correlation was found between these factors ($\beta''w_{p,n} - \sigma_y$: $R^2>0.86$; $\beta''w_{p,n} - \Delta H$: $R^2>0.81$).

Thesis 2 The influence of softening agent content is reflected by the specific yielding-related essential work of fracture ($w_{e,y}$) well both in the as received and rejuvenated state. The plasticizer (NPGDB) content leads to a small increase in $w_{e,y}$ until 10 wt%, while at 20 wt% the additive behaves as a real plasticizer and $w_{e,y}$ decreases as expected. The following relation can be given:

$$w_{e,y} = a \cdot \sigma_y + b,$$

where a and b are constants related to the material and ageing state. The value of a is 0.0003 m before rejuvenation, b is 0.2 kJ/m², while in the state after rejuvenation the value of a is 0.00025 m, and b is 0.

Thesis 3 In wet conditions the physical ageing of polymers slows down due to the constant presence of water that leads to softening and this was proven with the change in enthalpy relaxation. As a result of 264 hours of ageing enthalpy relaxation becomes 4.5 times smaller in case of PETG ($\Delta H_{damp\ condition}=0.74$ J/g; $\Delta H_{dry\ condition}=3.33$ J/g), and 9 times smaller for PET ($\Delta H_{damp\ condition}=0.51$ J/g; $\Delta H_{dry\ condition}=4.55$ J/g) compared to the rejuvenated values of the same material that was dry aged.

Thesis 4 For the first time in the literature I showed experimentally for the examined polyesters (PET, PETG) that there is a good correlation between the essential work of fracture (w_e , w_{TE}) determined in loading type I (In-plane, DEN-T specimen) and loading type III (Out-of-plane, trousers specimen). The reason for this phenomenon is that in case of loading type III when the shearing (trousers) type specimens are continuously loaded, the territory around the crack tip turns into the plane of loading type I.