

Relationships between molecular and plane-stress essential work of fracture parameters in amorphous copolyesters

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SUMMARY

The plane-stress fracture toughness of amorphous copolyester (aCOP) sheets of different intrinsic viscosity (IV) was determined by the essential work of fracture (EWF) concept using tensile-loaded deeply double-edge notched (DDEN-T) specimens. It was found that the specific essential work of fracture (w_e) is a composite parameter: its constituents are related to yielding ($w_{e,y}$) and necking ($w_{e,n}$), respectively. The w_e values, and especially $w_{e,y}$ did not change as a function of IV. This finding along with the fact that the mean entanglement length of the aCOP series was constant, suggest that $w_{e,y}$ (which is related to the critical plane-strain toughness value) is likely dependent on the entanglement network. This assumption was reasoned by the observation that the plastic zone was completely recovered after annealing the specimen beyond the glass transition temperature (T_g). Recall that the shape recovery in case of cold-drawing (i.e. deformation below T_g) is controlled by the initial entanglement network structure in amorphous polymers.

1. INTRODUCTION

The assessment of fracture toughness of ductile polymers by concepts of the post-yield fracture mechanics (PYFM) is a great challenge nowadays. Among methods of the PYFM the essential work of fracture (EWF) is gaining acceptance due to its easy

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performance. The EWF approach makes a difference between the essential (W_e , required to fracture the polymer in its process zone) and non-essential or plastic work (W_p , consumed by various deformations in the surrounding plastic zone). The total work of fracture (W_f) is composed of the two above terms:

$$W_f = W_e + W_p \tag{1}$$

Since W_e is surface-, whereas W_p is volume-related, W_f can be given by the related specific terms (i.e. w_e and w_p , respectively):

$$W_f = w_e \cdot l \cdot t + \beta w_p l^2 \cdot t \tag{2}$$

$$w_f = \frac{W_f}{l \cdot t} = w_e + \beta w_p l \tag{3}$$

where l is the ligament length, t is the thickness of the specimen and β is the shape factor of the plastic zone (cf. Figure 1). In respect to the EWF approach and its use for polymers the interested reader is addressed to refs. [1-5].

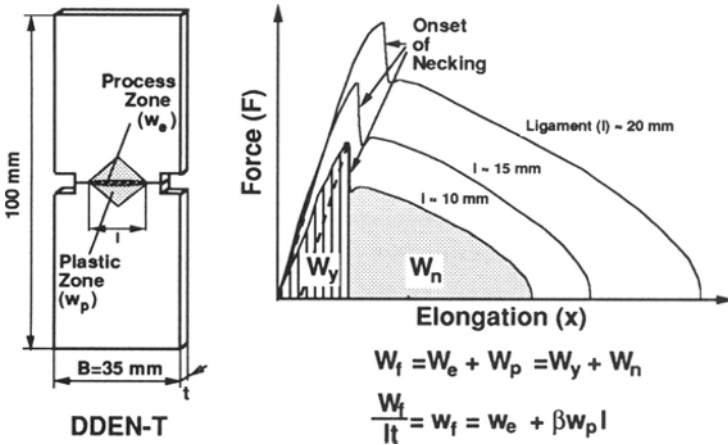


Figure 1
Designation and size of the specimens along with the related F-x curves

Basic questions in respect to w_e are: i) does this parameter represent the inherent material toughness, and ii) how does it depend on molecular characteristics? As far as the authors know no correlation between w_e and polymer characteristics (e.g. molecular mass, entanglement density, density of tie molecules) was disclosed.

This work was aimed at studying the relationships between w_e and molecular parameters in amorphous copolyesters (aCOPs).

2. EXPERIMENTALS

Materials and Their Characteristics

The aCOPs were synthesised from dimethyl terephthalate (DMT) and two diols: ethylene glycol (EG) and 1,4-cyclohexane dimethanol (CHDM). The amount of the latter was 31 mol %. The inherent viscosity (IV) of the aCOP was determined in 0.5 g/100 ml solution of 60/40 phenol/tetrachloroethane mixture at 25 °C.

The thermal response of the aCOPs was studied by modulated differential scanning calorimetry (MDSC). The MDSC traces were registered by a module of TA Instruments at heating rate of 5 °C/min superimposed by a sinusoidal heating-cooling profile of ± 2.45 °C/min.

FT-IR spectra were taken in transmission mode by an IR microscope (NicPlan, Nicolet). MDSC and FT-IR were adapted to study the deformation mode in the plastic zone of the specimens (see later).

Tests

For the EWF study double deeply edge-notched tensile (DDEN-T) specimens were cut from the thin sheets with a thickness (t) of ≈ 0.5 mm (cf. Figure 1). The testing conditions of the DDEN-T specimens along with the in-situ mapping of the emitted heat during deformation by infrared thermography (IT) were described in our previous works [6-7].

3. RESULTS AND DISCUSSIONS

3.1. Molecular Characteristics

Apart of IV (being a reliable and simple measure of the viscosity average molecular mass) a further molecular parameter, viz. the molecular mass between entanglements (M_e) was also considered. From the viewpoint of fracture of amorphous polymers the entanglement network, and its temperature- and time-dependent disentanglement behavior seem to be of crucial importance. It is known that M_e is constant for a polymer of the same composition beyond a given threshold molecular mass. For the aCOP series studied $M_e = 3260$ g/mol was deduced based on the plateau modulus in the molten state [8].

3.2. Essential Work of Fracture Parameters and Their Dependence on Molecular Characteristics

It was demonstrated in our previous works [6-7] that the load-displacement (F-x) curves at different ligament length are similar and yielding is separated from the subsequent necking by a load drop (cf. Figure 1). At this point the whole ligament yields instantaneously, that was evidenced by IT. This F-x behavior allowed us [6-7] to differentiate between the specific work of fracture required for yielding (w_y) and that consumed by necking and fracture (w_n) - cf. Figure 1.

Figure 2 shows the contribution of yielding (subscript:y) and necking (subscript:n) to the work of fracture parameters. In this study, however, emphasis was put only on the essential terms, i.e. w_e , $w_{e,y}$ and $w_{e,n}$. Figure 2 makes clear that w_e is a composite term under plane-stress conditions ($w_e = w_{e,y} + w_{e,n}$).

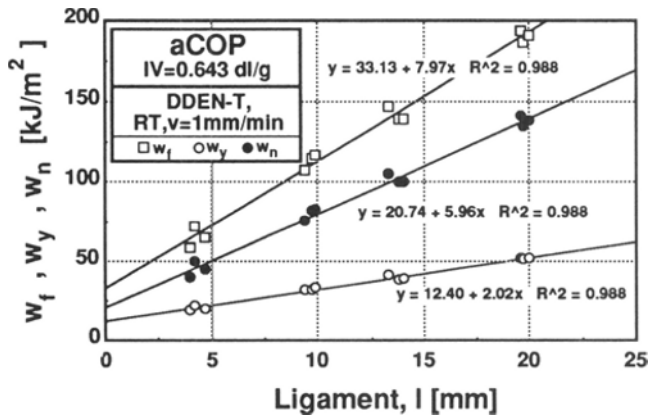


Figure 2
 w_f and its contributing terms (yielding, w_y and necking, w_n) vs l for an aCOP

The plots of the w_e terms (i.e. w_e , $w_{e,y}$ and $w_{e,n}$) as a function of IV are displayed in Figure 3. Figure 3 shows that w_e , $w_{e,y}$ and $w_{e,n}$ practically do not change in function of IV; this independence is especially clear for $w_{e,y}$ vs IV. This finding is of great scientific importance. Recall that $w_{e,y}$ is that EWF term which is closely matched with the plane-strain essential work fracture ($w_{e,Ic}$) [7]. $w_{e,Ic}$, representing an inherent material toughness parameter, seems to be independent on the mean molecular mass (or other related terms) in our case (cf.

Figure 3), but possibly dependent on the chain entanglement density. The entanglement density of the aCOPs studied was, however, constant so that no change in $w_{e,y}$ should be expected. The results in Figure 3 suggest indirectly that the work required to fracture an amorphous polymer in its process zone likely depends on characteristics of the molecular entanglement network. In order to substantiate this assumption first the yielding and necking mechanisms should be understood. It is obvious, however, that the suggested dependence of the w_e terms in function of the entanglement density requires further investigations with polymers of various entanglement characteristics.

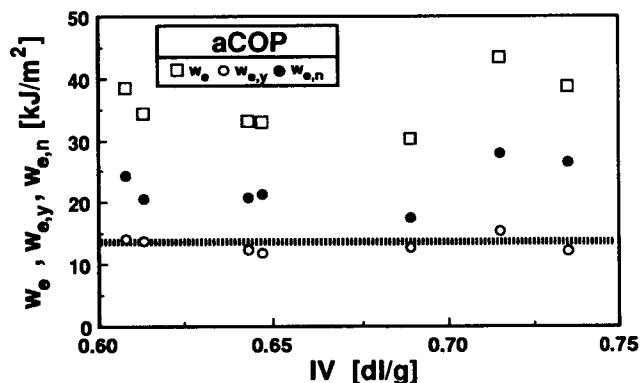


Figure 3
 w_e parameters vs
IV for the aCOPs
studied

3.3. Failure Mode in the Plastic Zone

It is known that aCOP grades are prone for crystallization in the molten state [7,9]. It was therefore checked whether or not necking was accompanied with strain-induced crystallization. FT-IR spectra taken from the bulk and plastic zone of the DDEN-T specimens are shown in Figure 4. In the IR-spectra no shifts in the absorption bands, related to conformational changes due to crystallization [10-11], can be revealed.

A further attempt was made to exclude the onset of crystallization. Figure 5 compares the MDSC traces of samples taken from the bulk and necked region of an aCOP. The middle, upper and lower MDSC traces in Figure 5 represent the conventional (C) and its reversing (R) and non-reversing (NR)

components, respectively. For the bulk sample (Figure 5a) the T_g can be found at ca. 76 °C (C and R curves). The peak in the NR component at ca. 73°C indicates for some physical ageing, whereas the origin of the broad endotherm at ca. 200 °C is unknown (Figure 5a). The sample from the necked region (Figure 5b) does not evidence crystallization or melting. The endothermic peaks at ca. 78°C and 56 °C in the NR curve can be assigned to physical ageing and orientational relaxation.

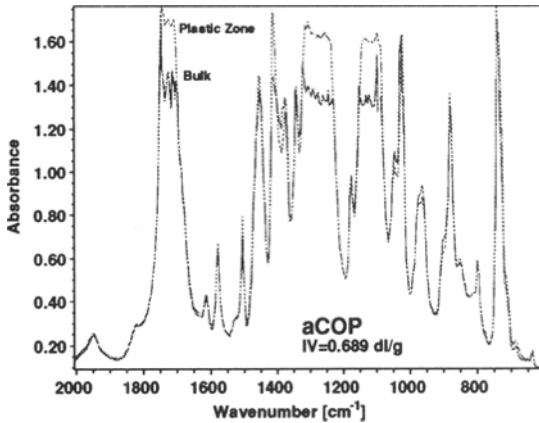


Figure 4

Comparison of the FT-IR spectra taken from the bulk and necked area of a DDEN-T specimens of an aCOP

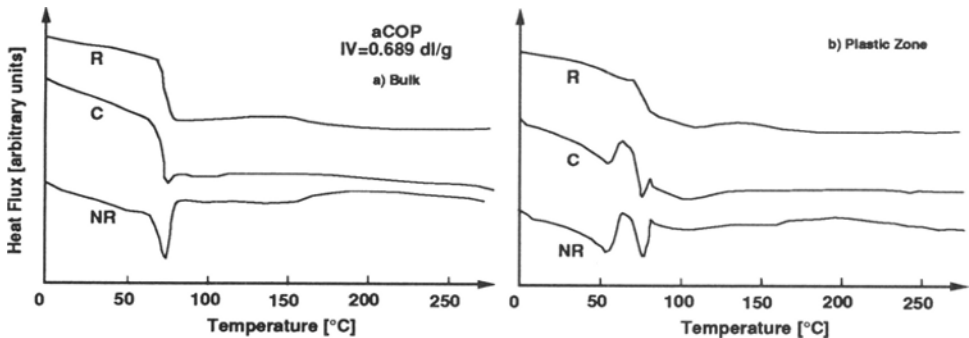


Figure 5

MDSC traces of samples from the bulk (a) and necked region (b) of a failed DDEN-T specimen of aCOP (IV=0.689 dl/g)

As demonstrated by IT frames in our earlier works [6-7], a substantial temperature rise accompanies yielding. Therefore the following question arises: does the local temperature exceed the T_g ? If yes, an irreversible plastic deformation should take place. This, however, can be excluded based on the FT-IR and

MDSC results. By keeping the broken DDEN-T specimen for few minutes just above the T_g (T_g of this aCOP is 90 °C), the plastic zone diminished and the shape of the specimen was fully restored, "healed" (Figure 6).

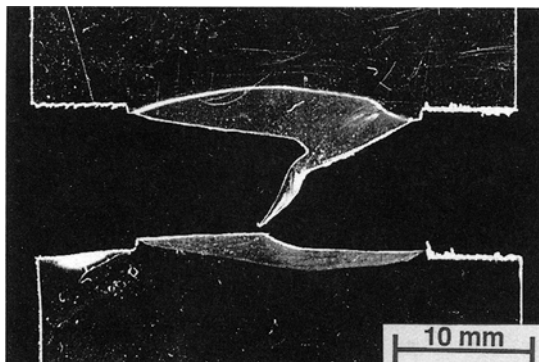


Figure 6

Macrophotograph taken from the plastic zone of a broken DDEN-T specimen of aCOP before (upper side) and after annealing (lower side) just above T_g ($T=100$ °C, 10 min)

Note: for demonstration purpose a DDEN-T specimen of unusual fracture behavior (see torn section) has been selected

This shape recovery in Figure 6 demonstrates that neither the T_g was reached nor a substantial change in the initial entanglement network structure occurred due to loading. Recall that the existence of the latter is the driving force for this memory effect [12-13]. The recovery of the initial shape of the DDEN-T specimens is the evidence that cold-drawing, and not true plastic flow, took place in the plastic zone of this aCOP. Based on this finding hardly any change in the w_e parameters can be expected, which was the case (cf. Figure 3), in fact.

4. CONCLUSIONS

The molecular relation of the plane-stress fracture behavior of aCOPs was studied by the EWF approach. As molecular parameters the intrinsic viscosity (IV) and the mean entanglement length (M_e) were considered. Based on this study, focussed on the specific essential work values, the following conclusions can be drawn:

- i- the specific essential work of fracture (w_e) is a composite parameter under plane-stress conditions. w_e could be separated to constituents relied on yielding ($w_{e,y}$) and necking ($w_{e,n}$). This separation was possible due to a characteristic load drop in the force-displacement (F-x) curves which marked when the yielding process was completed.
- ii- the w_e terms, and especially $w_{e,y}$ did not change as a function of IV. Therefore it was suggested that $w_{e,y}$ depends on the entanglement network density which was constant for this aCOP series. Though this suggestion was confirmed by showing that no true plastic deformation but cold-drawing took place during necking in the plastic zone, further investigations on aCOPs of various M_e are required to substantiate the suggested correlation. The complete recovery of the plastic zone upon annealing beyond T_g evidenced that the plastic zone was developed by a cold-drawing process in which the entanglement network was well preserved.

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