

DETERMINATION AND COMPARISON OF THE PLANE STRESS ESSENTIAL WORK OF FRACTURE OF THREE POLYESTERS PET, PPT and PBT

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The essential work of fracture (EWF) method has been used to study the relationship between molecular structure and thin film fracture toughness for three ductile polyesters at ambient temperature. The fracture toughness of PPT is of particular interest. Successful fracture characterisation of thin film polyesters has been achieved by the EWF method using double edge notched tension (DENT) specimens. The specific essential work of fracture, w_e , for polyethylene terephthalate (PET), polypropylene terephthalate (PPT) and polybutylene terephthalate (PBT) films is found to be 35.54 ± 2.56 , 41.03 ± 3.23 and 31.34 ± 8.60 kJ m⁻², respectively. Differential scanning calorimetry (DSC) has been employed to investigate the crystallinity of the polymers concerned and the effect of this on their EWF values.

Keywords: essential work of fracture (EWF), polyesters, PPT

Introduction

Progress in the medical device and packaging industries has been coupled to an increase in the design requirements of materials for these applications. Numerous engineering thermoplastics are currently used, but there is a constant search for new materials to fulfil ever more demanding design specifications [1–3]. Increasing use of thin film polyesters in high tension medical thin film and packaging applications has taken place in recent decades [4]. The greater demand for these applications has generated interest in methods that can be used to discriminate between the relative intrinsic toughness, or fracture resistance, of different polymers [5]; an example from the medical device industry being the angioplasty balloon catheter. Balloon angioplasty and stenting are successful alternatives to open heart surgery in treating arterial stenosis or blocked arteries [5–7]. Angioplasty balloons with wall thicknesses of 25–200 μm are typically exposed to pressures exceeding 1.5 MPa [5, 6]. Identifying a method for determining materials with optimal crack growth resistance, or intrinsic fracture toughness, is important in the development of these products [5].

Traditional fracture mechanics, that is to say, linear elastic fracture mechanics (LEFM) are inappropriate when characterising fracture in thin film ductile polymers, where crack propagation is associated with large plastic deformation in the region around the propagating

crack tip [8, 9]. The importance of designing materials that resist ductile fracture has resulted in the emergence of alternative elasto-plastic methods, like the J -integral, and the essential work of fracture used by designers and researchers over the past 40 years.

The J integral is the most popular method used to characterise the toughness of ductile metals and plastics. However, the technique demands that certain size requirements are met in test specimens. Indeed, the nature of deformation in plastic materials results in a significant variation in the measurements obtained for J , especially for specimens tested in the plane stress state [10]. Alternatively, the EWF method is enjoying increasing attention, with many workers adopting it in the characterisation of polymers [8–24]. The attractive features of the method are its theoretical purity and experimental simplicity [8, 9, 11]. The EWF method involves a more accommodating parameter for characterising the energy associated with ductile fracture. The technique provides a valid direct comparison of a fracture toughness parameter for polymeric materials (of same thickness) in the state of plane stress.

EWF theory

The EWF method was originally proposed by Broberg [25, 26] and has been elaborated by others, e.g. Cotterell *et al.* [27] who developed the nomencla-

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ture used in association with the technique. It is based on the concept of the separation of the energies of fracture, i.e., (i) those associated with elastic tearing in the region of the crack tip and (ii) those associated with far field plastic deformation at a distance away from the crack tip that does not contribute directly to fracture.

The total work of fracture, W_f , is the sum of the elastic energy and plastic energy contributions associated with deformation processes local to, and distant from, the propagating crack tip, respectively. W_f can be expressed as follows:

$$W_f = W_e + W_p \quad (1)$$

where W_e is the essential work of fracture and W_p is the non-essential work of fracture. The value of W_e is proportional to the fracture area and hence to the ligament length, l , for a given specimen thickness, t . On the other hand, W_p is proportional to the volume of the outer plastic zone. This volume is itself related to the square of the ligament length. Thus Eq. (1) may be rewritten as:

$$W_f = w_e l t + w_p \beta l^2 t \quad (2)$$

where w_e is the specific essential work of fracture, w_p is the specific non-essential work of fracture and β corresponds to a shape factor associated with the shape of the plastic zone. By reorganising the above expression, the specific total work of fracture, w_f , of a ductile material can be expressed by:

$$w_f = w_e + \beta w_p l \quad (3)$$

The elastic contribution, W_e , represents a material parameter that is independent of specimen geometry and the plastic component, W_p , is dependent on the shape and size of the plastic zone.

The critical stress intensity factor K_{Ic} , or critical strain energy release rate G_c , is only truly relevant to brittle fracture. The corresponding parameter used to describe the fracture toughness of ductile materials is J_c at crack initiation in the case of the J integral method. This value is represented by w_e when using the EWF approach.

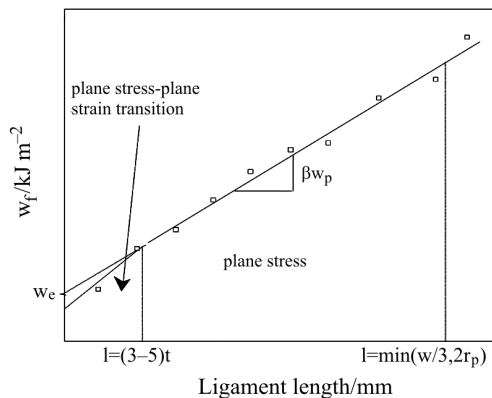


Fig. 1 Typical w_f vs. l plot for a ductile material

The EWF can be determined relatively simply by integrating the load-displacement (P - δ) curves for the ductile fracture of specimens of different ligament length. Plotting the specific total work of fracture w_f vs. the ligament length l , and extrapolating to zero ligament length yields the specific essential work of fracture. A typical plot is shown in Fig. 1.

Experimental considerations

When the condition of pure plane stress, or plane strain, is met w_f varies linearly with l . The condition for valid measurement is fulfilled for plane stress if the ligament length typically lies within a valid range of lengths; the lower limit for this range is 3 to 5 times the specimen thickness [11–21, 27, 28]. If the ligament length is lower than this limit a transition state from plane stress to plane strain occurs and the value of w_f becomes non-linear (Fig. 1). There is also an upper boundary for the valid ligament length (Fig. 1). Its value is commonly found to be one third the width of the specimen, w , or twice the plastic zone size, r_p , whichever is smaller [11–21, 27, 28]. The former condition ($l \leq w/3$) ensures that the size of the plastic zone is not altered by edge effects. Complete yielding of the ligament prior to its failure is accomplished by fulfilling the latter condition ($l \leq 2r_p$). The size of the plastic zone r_p is given by the following equation:

$$2r_p = \frac{E w_e}{\pi \sigma_y^2} \quad (4)$$

where E is the Young's modulus and σ_y the yield stress.

Besides the ligament length restriction another condition is necessary to ensure a state of plane stress. In the case of DENT specimens, the state of pure plane stress is reached when the net-section stress at maximum load, σ_n , lies below 1.15 σ_y [11, 13–17, 20–22, 28, 29]. The following equation can be used to calculate σ_n :

$$\sigma_n = \frac{P_{\max}}{tl} \quad (5)$$

where P_{\max} is the maximum load recorded at the yield point.

The value of σ_n increases when the ligament length shortens [11, 15, 17, 19–21] and the stress state moves towards a condition of plain strain. It should, however, be mentioned that both conditions are not essential and can be too restrictive, as is observed in many published articles [11, 14, 16, 17].

DENT geometry is preferred to single edge notched tension (SENT) geometry. Hashemi [11] explains that, in the case of DENT specimens, the necking of the ligament area and crack propagation occur after full yielding. Conversely, in the SENT geometry, crack

growth can occur before the maximum load is reached. Mai *et al.* [23] state that the SENT geometry can lead to specimen rotation as the load is applied in which case the ligament would not be evenly loaded; the yielding can spread to the outer edge of the specimen. In the case of DENT samples, the yielding is balanced and contained within the notched central section.

Thin film applications

Ultra-thin films can be achieved with PET and the material is commonly employed in packaging applications, including Mylar[®], as well as for use in thin-walled medical devices, for example in angioplasty balloon catheters.

Previous research

The fracture toughness of PET and PBT have been studied extensively by others [11–13, 16–21, 23]. However, data on PPT has not appeared in the literature to date.

Hashemi [12], in his studies on PET, confirms that w_e is a material constant at each given thickness, while βw_p is dependent on the specimen geometry. The apparent toughness of PBT is influenced by specimen geometry [11] and determinations using SENT specimens appear to produce higher βw_p values relative to DENT samples. Chan *et al.* [13] have also investigated the specimen geometry in relation to the fracture toughness of PET using the EWF method.

In the case of PBT, w_e is found to increase slightly as the test speed increases whilst βw_p values decrease [16]. The specific essential work of fracture of PET is found to be independent of the loading rate and specimen width [13].

No significant variation in the specific essential work of fracture for SENT specimens of different specimen thickness is observed, although βw_p decreases as the latter increases [11, 16, 21].

The value of w_e is also found to be unaffected by the specimen shape or orientation [21]. In contrast, the specific non-essential work of fracture displays higher values for a fracture normal to the extrusion direction [21].

In the case of PBT, w_e appears to be independent of temperature up to the T_g region of the polymer and decreases at higher temperatures [17, 21]. Arkhireyeva *et al.* [19, 20] have used the same

method to study the effect of temperature on the fracture of PET. As in the case of PBT [17], w_e is also found to be independent of temperature below the material's T_g before reaching a maximum and then decreasing with increasing temperature [19]. The βw_p value also exhibits a maximum at the T_g . The specific essential work of fracture parameters can be separated into two parts; (i) those relative to yielding (first part of the P - δ curve) and (ii) those linked to necking and tearing (end part of the P - δ curve) [20]. It is observed that the latter process plays a more prominent role in the fracture of the specimen across the temperature range studied. The 'secondary' specific essential works of fracture compensate for each other: when one decreases, the other increases, keeping the overall w_e value constant.

Karger-Kocsis *et al.* [24] have compared the fracture toughness of three amorphous copolyesters possessing different entanglement densities using the EWF method. The authors observe different tendencies for cold crystallisation in these materials, which influence the measurement of their intrinsic toughness.

Experimental

Materials

All polyesters were pure resins with no fillers or additives. The polyethylene terephthalate (PET) used was a commercial grade Melinar TS5 LASER+[®] obtained from Dupont Polyester (Wilton, Redcar, UK) with an intrinsic viscosity (*i.v.*) value of 0.84 dL g⁻¹. Polypropylene terephthalate (PPT) (or polytrimethylene terephthalate) was obtained from Shell Chemicals Belgium S.A. (Louvain-la-Neuve, Belgium). Its commercial grade name is Corterra[®] CP509211 (*i.v.*=0.92 dL g⁻¹). Polybutylene terephthalate (PBT) was received from Bayer A.G., Germany. The grade chosen was Pocan[®] B1300 (*i.v.*=0.95 dL g⁻¹). Manufacturers' *i.v.* values were confirmed by dilute solution viscometry using an Ostwald U-tube viscometer and various solvent/temperature conditions (Table 1).

Specimen preparation

All sample polyesters were reduced to a fine powder using a lab top micronisation unit prior to compress-

Table 1 Conditions for the solution viscometry measurements

Material	Solvent	Test temperature/°C	Mark-Houwink constants		
			$K/\text{dL g}^{-1}$	a	reference
PET	<i>o</i> -chlorophenol	25	$4.25 \cdot 10^{-4}$	0.69	[30]
PPT	60:40 (v/v) phenol/tetrachloroethane	30	$5.36 \cdot 10^{-4}$	0.69	[31]
PBT	1:1 (v/v) phenol/1,2-dichlorobenzene	25	$4.37 \cdot 10^{-4}$	0.72	[32]

Table 2 Solution viscometry data

Material	<i>i.v.</i> measured/dL g ⁻¹	<i>i.v.</i> manufacturer/dL g ⁻¹	<i>M_v</i> measured/g mol ⁻¹	<i>M_v</i> manufacturer/g mol ⁻¹
PET	0.74±0.03	0.82	50000	58000
PPT	0.96±0.04	0.92	52000	49000
PBT	0.93±0.01	0.95	42000	43000

sion moulding in order to obtain thin films with optimum homogeneity. The materials were compression moulded using a heated press (Mackey Bowley International Ltd. C10888/98) at 260°C into films with a thickness corresponding to approximately 0.13 mm.

Specimens of given dimensions were cut for each type of test using an appropriate stencil and a precision cutting tool equipped with a fresh blade. In the case of the fracture tests, samples were prepared with dimensions of 45 and 50 mm. DENT specimens were produced by accurately cutting two aligned notches of various depths halfway down each side of the rectangular samples using the same cutting tool. An upper limit of $w/3$ was used as the ligament length range with the lower limit chosen to correspond to $5t$. The thickness (t) was assigned as equal to 0.30 mm. This ensured a safe lower limit value. The calculated valid ligament length range was:

$$1.5 \leq l \leq 15 \text{ mm}$$

For practical convenience the lower limit was chosen as 2 mm.

Ten different notch depths between the values 15 and 21.5 mm were chosen.

Specimens destined for the Young's modulus test were cut to the following dimensions: 20 mm in width and 130 mm in length.

Finally, in the case of the yield stress test, 35×50 mm thin film samples were prepared with which to perform a comparative test. Two half circles (20 mm in diameter) were punched half way down each side to form dumb-bell shaped specimens.

The exact thickness of each specimen was measured at five different points using a micrometer and the average value used in subsequent calculations.

Testing

All tests were carried out using a Lloyd LRX tensile testing instrument at a loading rate of 1 mm min⁻¹. The apparatus was connected to a computer running proprietary software (Nexygen from Lloyd Instruments Ltd.).

Batches of seven identical specimens were studied to obtain an average value for each test.

In the case of the fracture tests, the specimen was gripped at both ends by the jaws of the instrument, leaving a gauge length of 30 mm, and the P - δ curve recorded. The energy associated with the P - δ curve for each specimen determined by the software was divided by the loaded area giving its total specific work

of fracture, w_f . Average w_f values for the ten different ligament lengths were plotted vs. l and values for both w_e and βw_p were obtained.

The P - δ curve for each strip of thin film used for the determination of the Young's modulus was also recorded. Proprietary software was used to calculate the slope of the initial linear relationship between P and δ , and the corresponding value for E was determined from the specimen's average thickness and other dimensions.

A similar P - δ curve was obtained for each dumb-bell shaped specimen. The comparative yield stress value was simply deduced from the maximum load value appearing on the plot at the yield point.

DSC analysis

The three polyesters were examined using a Perkin Elmer DSC 7 analyser equipped with a refrigeration cooling system. Thin-film samples (10 mg) were heated from -30 to 290°C at 20°C min⁻¹.

Results

Solution viscometry results

The data obtained from measurement of the *i.v.* for the three polyesters are given in Table 2. Viscosity average molecular mass, M_v , values have been calculated using the Mark-Houwink equation and the corresponding constants (Table 1).

The slight discrepancy between measured *i.v.* values and those quoted by the corresponding manufacturer are attributed in part to unavoidable reproducibility issues between laboratories. Moreover, the supplier's figures are average values for the materials in question. Different batches may also display slightly different *i.v.* values. Overall, the polyesters exhibit similar viscosity average molecular masses.

Tensile tests results

Polyester tensile test results are given in Table 3.

Table 3 Mechanical test results for the three polyesters

Material	<i>E</i> /GPa	σ_y /MPa
PET	1.62±0.11	42.7±1.5
PPT	1.25±0.11	33.9±2.5
PBT	0.953±0.075	25.7±1.5

Fracture tests results

Results for the fracture testing conducted on PET, PPT and PBT are shown in Figs 2–4, respectively.

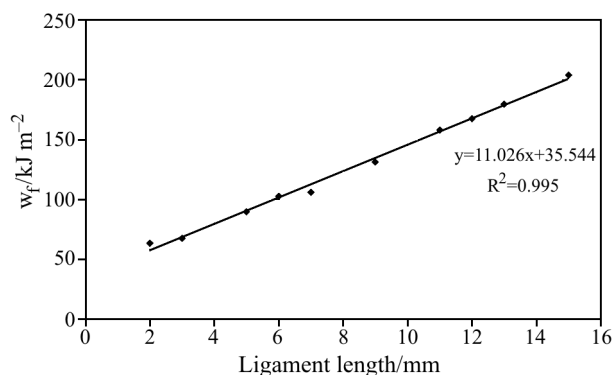


Fig. 2 w_f vs. l plot for PET

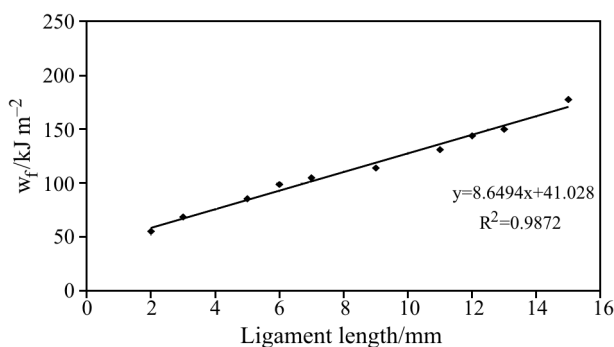


Fig. 3 w_f vs. l plot for PPT

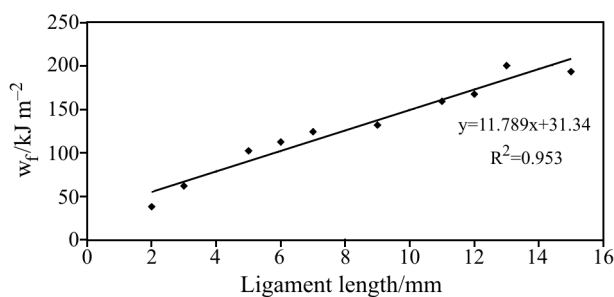


Fig. 4 w_f vs. l plot for PBT

The specific essential and non-essential work of fracture values are given in Table 4, along with those for the plastic zone size.

Table 4 Fracture test results for the three polyesters

Material	w_e /kJ m ⁻²	βw_p /MJ m ⁻³	$2r_p$ /mm
PET	35.54±2.56	11.03±0.276	10.1±1.1
PPT	41.03±3.23	8.649±0.348	14.0±2.4
PBT	31.34±8.60	11.79±0.926	14.4±4.3

DSC analysis

DSC traces for PET, PPT and PBT samples are displayed in Figs 5–7, respectively.

The glass transition peaks present in the DSC determinations of PPT and PBT are due to enthalpy of relaxation. ‘Physical ageing’ occurred in the time interval between mechanical testing and DSC analysis. This is not apparent in the case of PET because of its higher T_g value.

DSC data are used to calculate the apparent level of crystallinity within each sample. Using a method similar to that reported elsewhere [33], the enthalpy difference, ΔH_d , between the melting process and any recrystallisation event on heating each specimen is compared with the known enthalpy of fusion, ΔH^0 , of the polymer. Alternative methods (XRD, FTIR, density) can be used to generate a crystallinity index instead. Values of ΔH^0 for these materials are found in [34]. Table 5 presents these results.

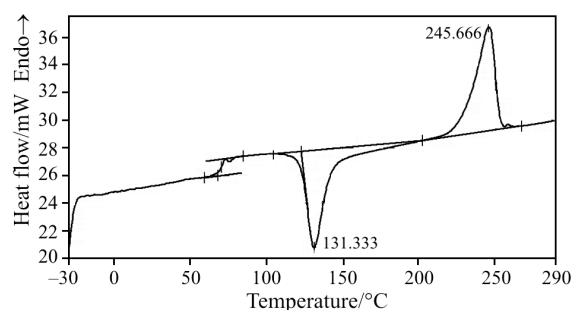


Fig. 5 DSC heating trace for PET

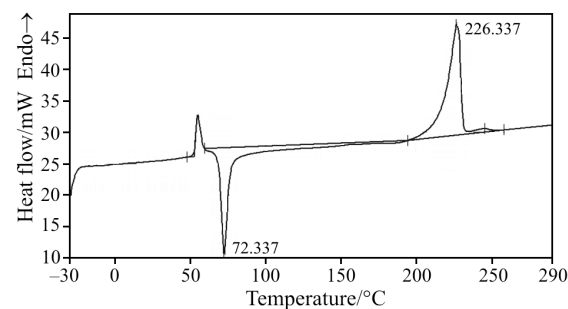


Fig. 6 DSC heating trace for PPT

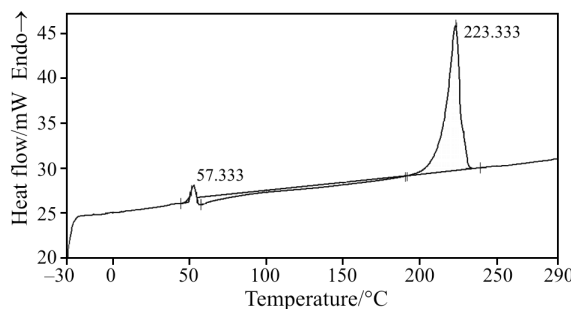


Fig. 7 DSC heating trace for PBT

Table 5 Apparent level of crystallinity of the polyesters

Material	$\Delta H_d/J\ g^{-1}$	$\Delta H^0/J\ g^{-1}$	Apparent level of crystallinity/%
PET	0	140	0
PPT	10	145	7
PBT	39	145	27

Discussion

As expected, and similar to the findings reported by Hwo *et al.* [22], the modulus and comparative yield stress values for PPT occur mid-way between those of PET and PBT (Table 3). The basis for this resides in the molecular structure of the polyesters concerned. Possessing only two methylene groups in its backbone chain PET is less flexible and more resistant to stretching than either PPT or PBT. With increasing numbers of methylene groups in both PPT and PBT the elastic modulus value can be expected to decrease and this is observed. In the case of comparative yield stress values, the same behaviour occurs, i.e. the tensile yield stress of PET is greater than PPT, which, in turn, is greater than for PBT.

There is no data available in the literature concerning the essential work of fracture of PPT. Indeed, the intrinsic toughness of the polymer has not been reported. Nevertheless, it is anticipated that the intrinsic toughness of PPT would be of the same order and/or lie between the values obtained for PET and PBT of similar molecular mass. Fracture toughness measurements obtained for thin film specimens are similar to values that have been reported for PET elsewhere [12, 13, 18–20, 23]. Hashemi [12] has obtained values for w_e and βw_p corresponding to 30.50 kJ m⁻² and 10.20 MJ m⁻³, respectively, involving samples of equivalent thickness (0.125 mm) with a yield stress value of 85 MPa. Karger-Kocsis *et al.* [24] cite values of 45.7 kJ m⁻² for w_e and 9.9 MJ m⁻³ for βw_p corresponding to a PET sample 0.5 mm thick with a yield stress value of 54.7 MPa. These differences, between the values previously published and those reported here, are most probably related to differences in the combined parameters such as sample thickness, rate of deformation, variances in macromolecular properties, etc.

In his studies on the work of fracture of PBT Hashemi observes w_e values of 36.25 kJ m⁻² [16] for specimens 0.175 mm thick with a yield stress of 43.25 MPa tested at 2 mm min⁻¹, and 36.97 kJ m⁻² [11] for thin film samples with a thickness of 0.125 mm, a yield stress value of 46.75 MPa and a width of 40 mm. The published w_e values are significantly greater than the figure of 31.34 kJ m⁻² reported in this work, however, both can be considered to constitute the same approximate order. To support this assertion it is necessary to note that values for the specific non-essential work also differ: 3.85 [16] and 2.62 [11] compared

to 11.79 MJ m⁻³ obtained for the material considered here. This discrepancy possibly originates from variations in the level of crystallinity for each grade of PBT (the PBT studied was quenched to limit its crystallisation) and would provide an explanation for the much higher βw_p value recorded for the sample considered here in comparison to the value reported by Hashemi [11, 16].

The βw_p value is not an intrinsic material property and depends on the fracture process zone which itself is sensitive to specimen geometry, ligament length and deformation rate. However, all three polyesters have been tested under the same conditions and a comparison between their βw_p values can therefore be made. The results show that the specific non-essential work of fracture, βw_p , of PPT is lower than for PET and PBT (Table 4); values for the latter two materials being very similar. In the case of PPT, plastic deformation contributes less to the total energy of fracture than for the other polyesters, illustrating that PPT possesses greater intrinsic toughness than PET and PBT.

Greatest interest arises when values for the specific essential work of fracture regarding the three polyesters are compared. It is predicted that PBT would exhibit lower toughness and stiffness than PET because of its molecular structure. This is confirmed by the tensile and fracture test results obtained (Tables 3 and 4) which demonstrate lower values for E , σ_y and w_e in the case of PBT. The linearity observed on plots of w_f vs. l for PBT, although satisfactory, is slightly poorer than for PET. This can be explained by the much faster crystallisation rate of PBT. Inevitably, each thin film sample of PBT exhibits a slightly different level of crystallinity and subsequently a different w_f value.

From its structure, PPT is predicted to possess a value of w_e intermediate to that of equivalent molecular mass material corresponding to PET and PBT. However, PPT displays the highest value out of the three materials tested with $w_e=41.03\pm 3.23$ kJ m⁻². This observation is reinforced by the fact that all three materials feature identical thermal histories, no orientation and similar molecular masses (Table 2).

PPT has been described as possessing better toughness than PBT and similar strength properties to PET [35]. The present work demonstrates that the resistance of PPT to fracture even exceeded that for PET for the particular grades of material and thermal histories encountered here.

All fracture tests have been conducted with samples in a state of plane stress, i.e. the net-section stress condition is always fulfilled. For each polyester, the average net-section stress has been calculated for every ligament length using Eq. (5). The net-section stress condition is illustrated in Figs 8–10 for PET, PPT and PBT, respectively.

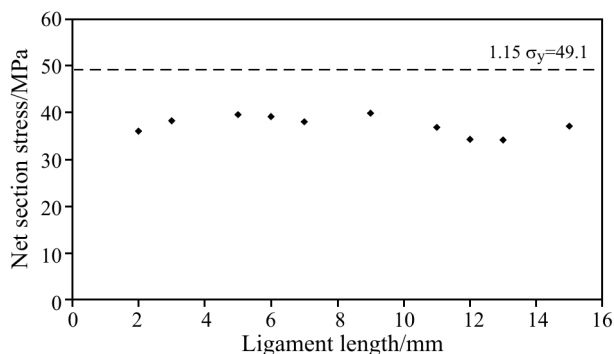


Fig. 8 σ_n vs. l plot for PET

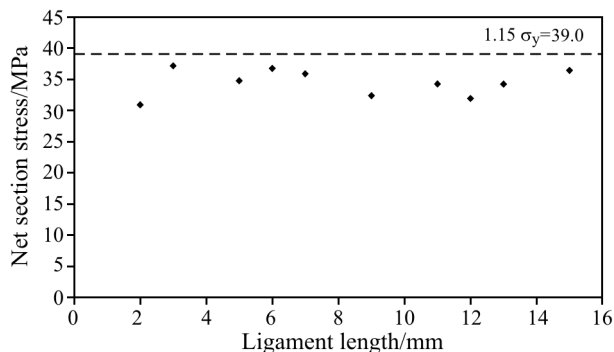


Fig. 9 σ_n vs. l plot for PPT

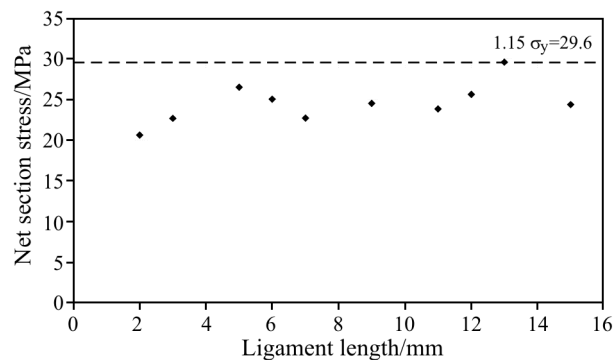


Fig. 10 σ_n vs. l plot for PBT

All σ_n values are lower than or equal to the $1.15 \sigma_y$ limit for each polymer.

After conducting the tests, the value of the plastic zone size has been calculated for each polymer using Eq. (4). These are given in Table 4. All three $2r_p$ values are lower than $w/3$ ($=15$ mm). However, the values are deemed too restrictive as an upper limit for l . Indeed, deviation from linearity is not recorded in the three plots of w_f vs. l (Figs 2–4) within the ligament length range comprising $2r_p$ and $w/3$. Consequently, in the case of each material tested, the upper limit for the ligament length has been chosen as $w/3$ (15 mm) and thus all ten sets of data are considered.

The DSC data (Table 5) demonstrate that PBT is the most crystalline of the three polyesters. By comparison, PET has a slower crystallisation rate, whereas PPT displays an intermediate apparent level of crystallinity. A crystalline polymer is expected to have better strength and stiffness, i.e. higher E and σ_y values, than an amorphous polymer. The fracture toughness of a polymer is also dependent on its crystalline content. As PPT exhibits a higher apparent level of crystallinity than PET this may explain the higher w_e value; although this observation could also originate from differences in the fundamental molecular structures of the two polyesters. Conversely, PBT exhibits the lowest specific essential work of fracture value despite displaying the highest level of crystallinity. The validity of the explanation for the highest w_e value, in the case of PPT, being due to differences in crystalline content is therefore questionable. However, it is possible that the more highly crystalline polyester, PBT, had resulted in a brittle macromolecular state and thus exhibited lower fracture toughness in due course.

Conclusions

This research compares the fracture toughness of three closely related polyesters. The modulus and yield stress values of these materials obey the following expected order: PET>PPT>PBT. Interestingly, the specific essential work of fracture did not exhibit the same tendency. Indeed, PPT possesses the highest w_e value of 41.03 ± 3.23 kJ m⁻², followed by PET at 35.54 ± 2.56 kJ m⁻² and PBT at 31.34 ± 8.60 kJ m⁻². DSC analysis reveals different apparent levels of crystallinity for the three polyesters, despite comparable methods of preparation. This is expected as the polymers exhibit different crystallisation rates while undergoing identical processing conditions. It is uncertain whether or not these differences are the origin of the disparity between the specific essential work of fracture values for the polyesters studied.

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