The influence of a multilayer structure on the fracture of polyester film

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Recently we have measured the toughness of a multilayer film based on poly(ethyleneterephthalate), (PET) by two tear methods and found it to be greater than that expected from work elsewhere and in contrast to that predicted from a simple rule of mixtures.

Fracture studies have shown for a range of material types, that when an underlying multilayer or laminate structure is present, it can often confer synergistic levels of mechanical strength or toughness [1–3]. The phenomenon has been exploited using polymeric materials and has usually involved the generation of multiple layers which alternate in composition. Thus by employing two component polymers with contrasting physical properties and by fabricating a structure of alternating layers numbering from tens to hundreds, notable improvements have been reported in fracture toughness, tensile strength and ductility [4–7].

However the choice of fracture test is also important. Its geometry dictates the mode of deformation at the propagating crack front and thereby the specific response of the component materials. Consequently the material combination and multilayer architecture which provides optimum toughness will vary depending on the nature of the test. For example ductile yield and extended plastic deformation by film from PET under simple tensile strain is enhanced by the insertion of layers from poly(ethylenenaphthalate), (PEN) which has a slightly higher modulus [4]. In contrast it is reported that increased toughness, derived from energy to fracture by tearing is achieved for the film when a multilayer structure is constructed using a second polymer whose modulus is a fraction of that of PET [5].

Recently, during an examination of the optical properties of film from PET which contained a dispersion of inorganic particulate, barium sulphate, ($BaSO_4$) we noted an exception to the latter case.

Commercial film from PET homopolymer is widely reported, it is biaxially oriented, transparent and tough [8]. However film containing $BaSO_4$ is opaque and white, with similar modulus and tensile strength but lower toughness than its unfilled counterpart. These contrasting properties arise due both to the presence of the inorganic additive and to cavitation which develops in the PET matrix, around the filler particle during the stretching or drawing stages of the film process. As part of an investigation into the effect of a multilayer structure on the opacity of a film we prepared samples comprising discrete layers from the two materials based on PET. However, since the individual monolayer films from each material possess similar moduli, no significant change in tear toughness was anticipated.

Film was produced on a pilot scale biaxial film process during two separate production campaigns. The two polymers, PET and PET containing 18% by weight $BaSO_4$, were processed using a coextrusion system and a multilayer structure generated in the coextruding melt by sequentially splitting and recombining the melt flow [9]. After casting, the multilayer film was stretched in the machine and transverse directions by factors of approximately $\times$ 3.1 and $\times$ 3.2 respectively, and finally heat set above 200°C [8]. Film comprising 9 layers was produced with an overall thickness around 80 μm. Table I describes the conditions used to prepare the film, using different relative rates of the two coextrusion flows, a series of compositions were produced in which the layer

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TABLE I. Properties of multilayer and monlayer film

Film	Number of layers	Extrusion Feed Rate[a] Stream 1 (kg h^{-1})	Stream 2 (kg h^{-1})	Total $BaSO_4$ (% by wt)	Graves tear toughness (MN m^{-2})	Standard deviation (σ)	Trouser tear energy (kJ m^{-2})	Standard deviation (σ)
Set 1								
1a	9	93	40	15.7	4.10	0.56	10.1	1.0
1b	9	71	48	13.1	6.03	0.46	14.0	1.5
1c	9	59	60	11.1	6.74	0.74	19.6	1.8
1d	9	50	75	8.6	9.19	1.79	18.5	0.9
1e	1	72	48	9.4	5.26	0.50	12.9	1.3
1f	1	72	48	11.1	4.84	1.22	11.3	0.3
1g	1	72	48	14.7	3.75	0.29	12.4	0.3
1h	1	72	48	18.7	2.57	0.14	10.1	0.3
Set 2								
2	1	100	–	0	8.24	0.64	16.5	5.5

[a]For films 1a–d and 2, extrusion stream 1 delivered PET, stream 2 PET containing 18% by weight $BaSO_4$.
For films e–h PET and modified PET were blended at discrete ratios and delivered by both streams 1 and 2.

thickness and the overall concentration of $BaSO_4$ were systematically varied.

For comparison, a number of monolayer films containing $BaSO_4$ were also prepared from physical blends of the two polyesters and on the second occasion monolayer film from unmodified PET was produced.

Optical microscopy was used to confirm the structure of each multilayer film and its overall content of $BaSO_4$ was determined after pyrolysis of a specimen and measuring the mass of the residual ash.

The toughness and fracture energy of each film was measured using two methods, the Graves tear test and the trouser tear test. Details of the measurements are described elsewhere [5, 10–12]. The toughness of film was derived from the plot of force against deflection of the Graves tear test, according to Bland [5], while the energy to fracture, w_e by the trouser method was calculated using the relation,

$$w_e = \frac{2F}{t}$$

where F is the load during stable tear and t the film thickness [12]. For both tear methods, the specimen of film was mounted such that the fracture propagated in the process or machine direction, (MD) of the film. In this way, the direction of the propagating crack was parallel to the plane of the film and its constituent layers, while the crack face was perpendicular to both.

Details of the film produced for this study are also given in Table I and an example of the multilayer structure is shown in Fig. 1.

Table I reveals that at approximately similar overall levels of $BaSO_4$ additive, the change from the simple monolayer structure to the multilayer architecture is accompanied by a significant increase in Graves toughness. This is illustrated by the plot in Fig. 2. Here we show, the toughness of both types of film along with a line, predicted from a simple rule of mixtures, to depict the toughness

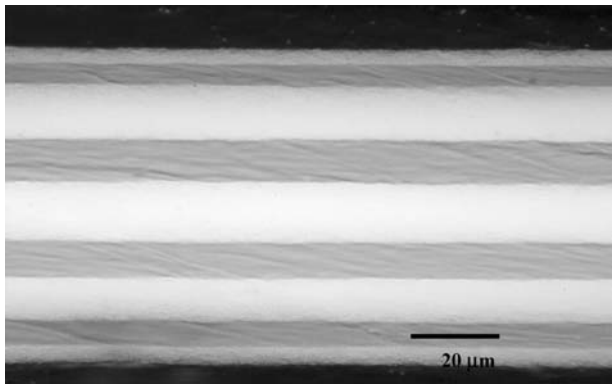


Figure 1 Multilayer structure of film 1c.

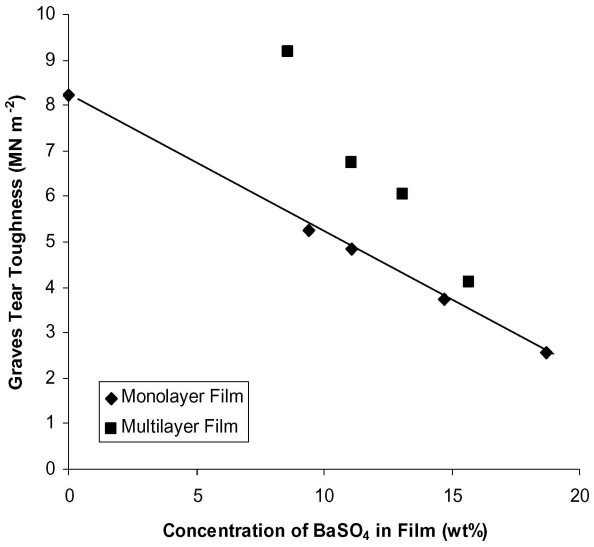


Figure 2 Graves tear toughness of film.

of film containing intermediate levels of $BaSO_4$. In principle this relationship can apply to both monolayer and multilayer sheets [13, 14].

Although the toughness of mono- and multilayer film is identical at additive concentrations of 0 and 18% by

weight because the structure of each film at those limits is identical, it is clear that at intermediate levels of $BaSO_4$, it is the monolayer construction which follows the rule of mixtures. In contrast, between the limits of additive concentration, the multilayer structure is clearly tougher than the equivalent monofilm, in some cases by almost a factor of two. A similar pattern is shown in Fig. 3 by the fracture energy recorded during the trouser test, again reflecting the influence of the multilayer architecture.

Although the differences in toughness here are not as great, Fig. 3 provides interesting information. Since the original objectives of the study did not require film with $BaSO_4$ loadings below 10% by weight, it is not possible to tell whether the multilayer structure in Fig. 2. does exhibit a tear toughness which exceeds that of the monolayer film structures from both component polyesters. However because of the small gradient of the drawn line in Fig. 3, it appears that, by the trouser tear test at least, it does.

The mechanism by which this toughening phenomenon arises is of course of key importance. In multilayer systems based on organic polymers, a complex interplay of structure and properties can operate, but careful scrutiny can resolve the fracture mechanisms.

For example strong interlayer adhesion can encourage cooperative yield and plastic flow to high strains while delamination can be advantageous to inhibit crack propagation across layers and premature failure [15]. Crack arresting may also occur in one layer if it can absorb energy or modify the cracktip zone.

However no fracture mechanism was offered for the case where the tear toughness of film from PET was enhanced by the presence of a second polymer [5]. Instead, the toughening phenomenon was demonstrated from data to occur if the modulus of the companion polymer was significantly lower than that of the PET. Layer dimensions also played a role.

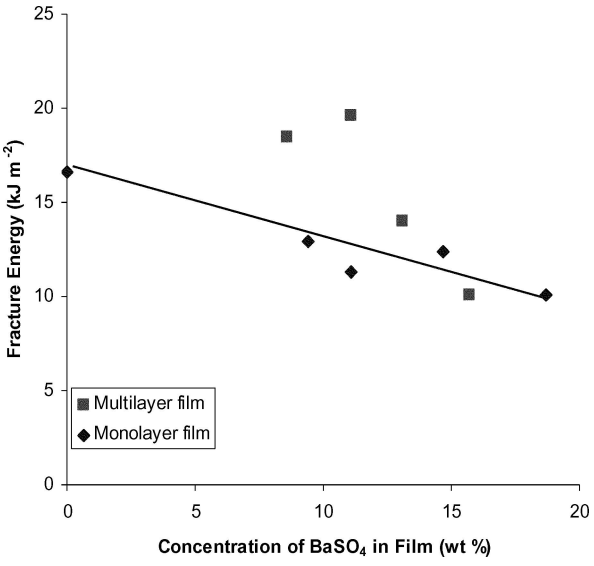
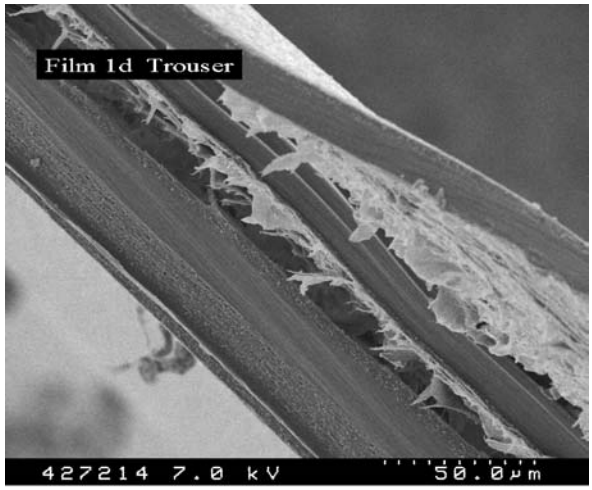


Figure 3 Trouser tear energy of film.

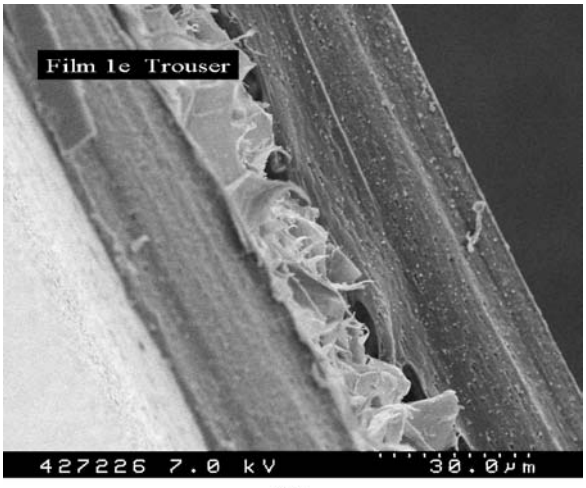
In the present work, no significant difference between the moduli of the component materials exists, thus a different mode to absorb energy during tear must operate. A preliminary examination of fracture surfaces after both Graves and Trouser tests indicated delamination has occurred. However in Fig. 4, at high magnification we see it is not delamination at the layer boundary but, cohesive failure within the layer of filled PET.

Although this failure is present in the monolayer film, examinations after repeated tests revealed only one fracture plane. In contrast two or more planes of fracture were counted in the corresponding multilayer samples. While this observation must be confirmed through additional fracture experiments, it seems that one contribution to the unexpected toughness of the polyester film is the greater area of fracture which occurs within discrete layers prior to final failure of the multilayer structure.

In summary, we have observed an increase in toughness, in film from PET containing $BaSO_4$ particles, due to the presence of a multilayer structure. This was unexpected since the moduli of the component materials which form



(a)



(b)

Figure 4 Electron micrograph of fracture surface from trouser tear: (a) Multilayer film 1d and (b) Monolayer film 1e.

the laminate structure are essentially identical. However the explanation appears to lie in cohesive failure of the particulate filled layers, during the tear test.

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