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Fatigue resistance of impact-modified thermoplastic copolyesters

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The effect of impact-modifier concentration and particle size on the fatigue resistance of an amorphous thermoplastic copolyester of dimethyl terephthalate with ethylene glycol and 1,4-cyclohexanedimethanol (KODAR®* PETG) was determined. Fatigue crack propagation (FCP) rate at a given value of stress intensity factor range, ΔK, decreased by a factor of four with the addition of an impact modifier, if the inherent viscosity of the PETG remained constant. The FCP rate did not vary with modifier concentration or particle size. However, the value of ΔK at instability did increase with increasing modifier content and particle size appeared to alter the FCP mechanism. In fatigue tests on unnotched specimens, neat PETG was more fatigue resistant than the impact-modified blends, suggesting that the modifier particles reduced the number of cycles required to initiate a crack.

1. Introduction

It is well known that the impact resistance of glassy thermoplastics can be dramatically enhanced by the addition of a rubbery phase or "impact modifier" [1, 2]. Numerous studies have shown that the effectiveness of an impact modifier depends on, among other things, concentration and particle size [1–4]. However, relatively little is known about the effects of these parameters on the fatigue resistance of glassy thermoplastics. Previous work by this author showed that in a miscible amorphous blend of polycarbonate and a copolyester of dimethyl terephthalate with ethylene glycol and 1,4-cyclohexanedimethanol, the addition of only 3 wt % of an impact modifier decreased the fatigue crack propagation (FCP) rate at a given stress intensity factor range, ΔK, by a factor of 20 [5]. Hertzberg and co-workers have shown that FCP rates at a given ΔK in poly(vinyl chloride) (PVC) and polystyrene also decreased with the addition of a rubber modifier [6–8]. In the toughened PVC blends, the addition of more than 6 wt % impact modifier, a methacrylate–butadiene–styrene rubber, had no additional effect on FCP rate. None of these studies, however, addressed the role of impact-modifier particle size on fatigue resistance. The objective of this work was to determine the effect of impact-modifier concentration and particle size on the fatigue resistance of an amorphous thermoplastic copolyester.

2. Experimental procedure

A thermoplastic copolyester of dimethyl terephthalate with ethylene glycol and 1,4-cyclohexanedimethanol (KODAR® PETG) was supplied by Eastman Chemical Company, Kingsport, TN. Two commercially available core–shell impact modifiers with average particle diameters of approximately 0.20 and 0.35 μm, designated PD20 and PD35, respectively, were used in this study. Blends of PETG with PD20 were first compounded into a concentrate containing 30%, by weight, of the impact modifier. The concentrate was then let down in a second compounding operation to give the final compositions. The additional compounding step was designed to increase dispersion of the modifier. Blends of PETG with PD35 were compounded in a single step. All compounding operations were performed on a Werner–Pfleider 28 mm twin screw extruder. Plaques were then moulded on a Toyo 90 injection moulding machine. The compositions of the blends used in this study and the inherent viscosity (IV) of the PETG component after moulding, are listed in Table I. The low inherent viscosity of PETG in the blends containing PD20 can be attributed to the additional compounding step discussed above.

FCP tests were performed on compact tension specimens, machined from 6.3 mm thick injection–moulded plaques, according to the diagram shown in Fig. 1. The specimens were notched in the mould-flow direction with a band saw. A razor blade was then tapped into the root of the notch, and a fatigue pre-crack was grown from the razor-sharpened notch prior to data acquisition.

FCP testing was conducted according to ASTM E647-91 [9] at ambient conditions on an MTS closed-loop servohydraulic testing machine using a sinusoidal waveform with a frequency of 10 Hz. All tests were conducted in load-control using a minimum-to-maximum load ratio of 0.1. Crack length was measured by computer, using an elastic compliance technique with a clip gauge mounted on the front face

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* KODAR® is a registered trademark of Eastman Chemical Company.

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TABLE I PETG blends used in this study

Composition (wt % impact modifier)	Inherent viscosity of PETG ($dl\,g^{-1}$)^a
0% (moulded only)	0.721
0% (extruded and moulded)	0.605
2.5% PD35	0.608
5% PD35	0.623
10% PD35	0.649
15% PD35	0.615
5% PD20	0.577
10% PD20	0.583
15% PD20	0.587

^{a}Measured in 60/40 phenol/tetrachloroethane at 23°C.

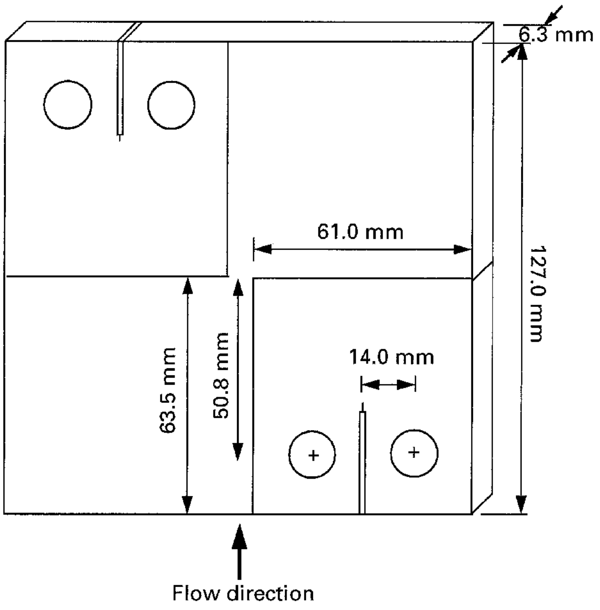

Figure 1 Diagram of compact tension specimens machined from injection-moulded plaques.

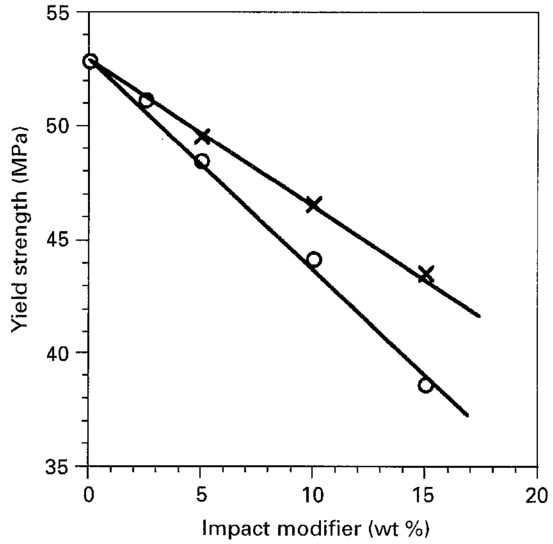

Figure 2 Tensile strength versus concentration of impact modifier for (○) PD35 (×) and PD20. Each data point represents an average of five specimens.

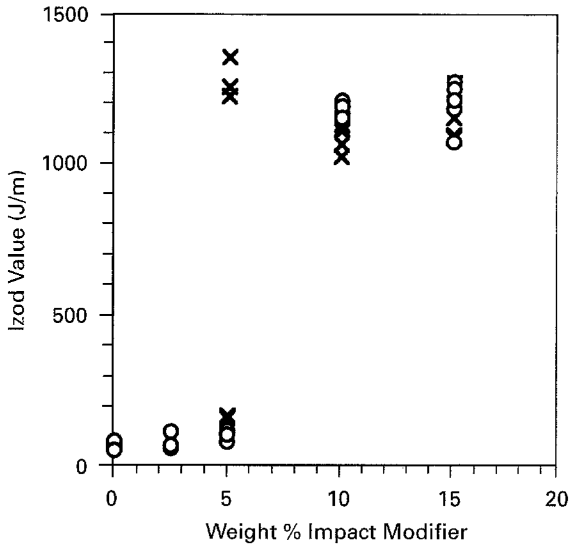

Figure 3 Izod number versus concentration of impact modifier for (○) PD35 and (×) PD20. Five specimens of each composition were tested.

of the compact tension specimen. FCP rate, da/dN, was computed by an incremental polynomial method and plotted versus ΔK according to the Paris law

$$da/dN = A\Delta K^m \quad (1)$$

where A and m are material parameters [10]. Stress intensity solutions, compliance coefficients, and details of the polynomial method are found in ASTM E647-91 [9]. Each set of FCP data shown in this work was recorded from one specimen only. Repeat experiments gave values of da/dN at a given value of ΔK that agreed to within $\pm$ 20%. Optical micrographs of the fracture surfaces were obtained by using a Wild M400 optical microscope.

Notched Izod impact tests were performed according to ASTM Standard D256-92 [11]. Tensile tests were performed according to ASTM Standard D638-91 [12] using a crosshead speed of 50.8 mm min^{-1}. Flexural fatigue tests on unnotched specimens were performed according to ASTM Standard D671-90 [13].

3. Results and discussion

Yield stresses and notched Izod values for PETG/PD20 and PETG/PD35 blends are shown in Figs 2 and 3, respectively. Yield stress decreases linearly with increasing modifier concentration in both sets of blends, although PD35 has a stronger effect on yield stress. In Izod tests, both sets of blends exhibit a brittle-to-ductile transition as impact modifier concentration is increased. In the PETG/PD35 blends, brittle failures occurred at concentrations of up to 5 wt % of the modifier. In the PETG/PD20 blends, however, a mixture of brittle and ductile failures occurs in blends containing 5 wt % of the modifier, suggesting that PD20 may be a slightly better impact modifier for PETG.

A log–log plot of da/dN versus ΔK for two neat PETG samples with different inherent viscosities is shown in Fig. 4. One sample (IV = 0.605) was extruded and moulded in order to match the processing history of the blends; the other sample (IV = 0.721) was only moulded. Clearly, IV has a strong effect on

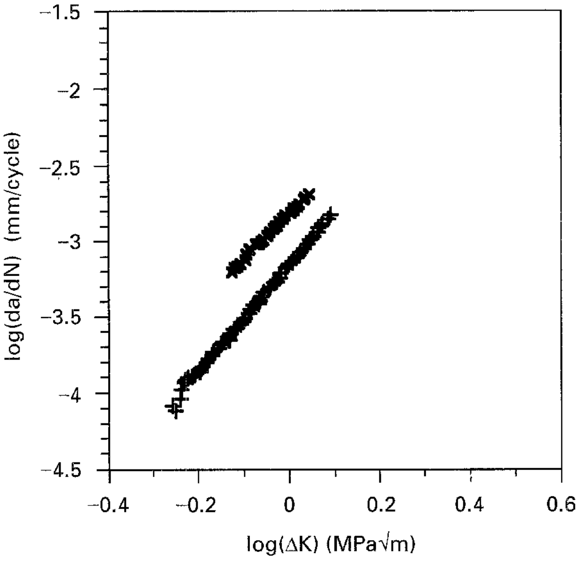

Figure 4 Log–log plot of da/dN versus ΔK for neat PETG with IV = (+) 0.721 and (×) 0.605.

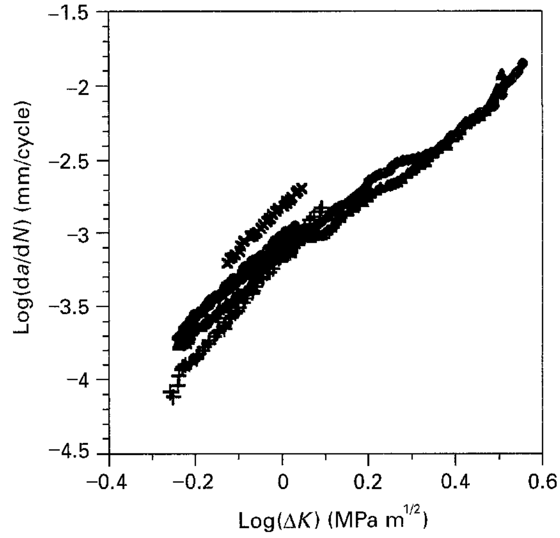

Figure 6 Log–log plot of da/dN versus ΔK for PETG/PD20 blends containing (●) 5%, (◆)10%, and (▲) 15% PD20. Neat PETG symbols are the same as in Fig. 4.

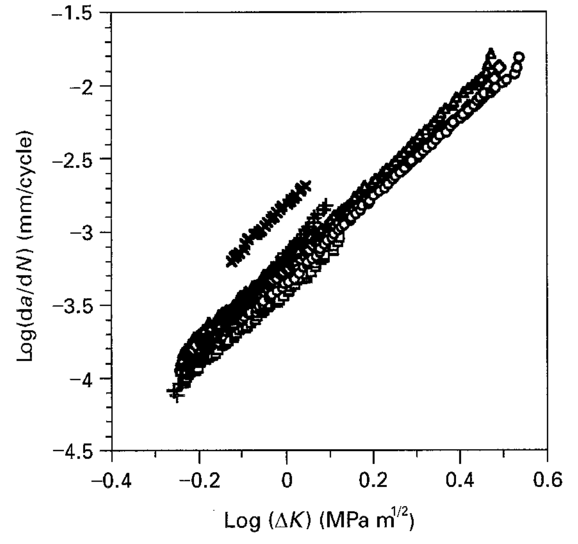

Figure 5 Log–log plot of da/dN versus ΔK for PETG/PD35 blends containing (□) 2.5%, (○) 5%, (◇) 10%, and (△) 15% PD35. Neat PETG symbols are the same as in Fig. 4.

da/dN; at any common value of ΔK, da/dN in the low IV sample is more than twice da/dN in the high IV sample. Furthermore, the value of ΔK at instability, ΔK_i, in the low IV sample is slightly less than ΔK_i in the high IV sample. Because the FCP rate in PETG is so sensitive to IV, the IV of PETG in the blends must be kept constant in order to evaluate properly the effect of impact modification on FCP behaviour.

A log–log plot of da/dN versus ΔK for PETG/PD35 blends is shown in Fig. 5. The IV of PETG in the blends is relatively constant and averages 0.62 (see Table I). The FCP data for the neat PETG samples, shown in Fig. 4, are also included in Fig. 5. FCP rates in the impact-modified blends are fairly independent of concentration and are approximately a factor of 4 lower than FCP rates in the neat PETG with a similar IV (IV = 0.605). In addition to lowering da/dN, impact modification increases ΔK_i substantially when the modifier concentration is at least 5 wt %. It should be noted that FCP rates in the impact-modified blends are approximately equal to FCP rates in the high IV (IV = 0.721) neat PETG, suggesting that the loss in IV due to the compounding operation is sufficient to offset the added fatigue resistance from impact modification.

A log–log plot of da/dN versus ΔK for PETG/PD20 blends is shown in Fig. 6. These results are similar to those described above for blends containing PD35. However, in these blends, at least 10 wt % of PD20 is needed to increase ΔK_i significantly, compared to only 5 wt % PD35.

Fatigue crack propagation in both sets of blends occurs by discontinuous growth band (DGB) formation. A DGB is a fracture-surface marking which corresponds to an increment of crack growth caused by multiple cycles. Optical micrographs of typical DG bands for neat PETG, and blends containing 5 wt % PD35 and PD20 are shown in Fig. 7. The number of cycles per DGB at a given value of ΔK can be determined by comparing DGB size with the macroscopically determined FCP rate (Figs 5 and 6). Fig. 8 shows a plot of the number of cycles per DGB as a function of ΔK. Data from the two sets of blends form two distinct sets of curves. At a given value of ΔK, fewer cycles are needed to form DG bands in the blends containing PD20 than in the blends containing PD35. In both sets of blends, however, the number of cycles per DGB decreases with increasing ΔK. In neat PETG, fatigue crack propagation occurs by DGB formation at low values of ΔK and by striation formation (a fracture-surface marking which corresponds to an individual cycle) at high values of ΔK. The number of cycles per DGB in neat PETG closely follows the behaviour of the PETG/PD20 blends (see Fig. 8).

Hertzberg and Manson [6] have shown that an effective yield stress of a material may be determined as a function of ΔK if one assumes that the DGB width represents the size of the plastic zone preceding

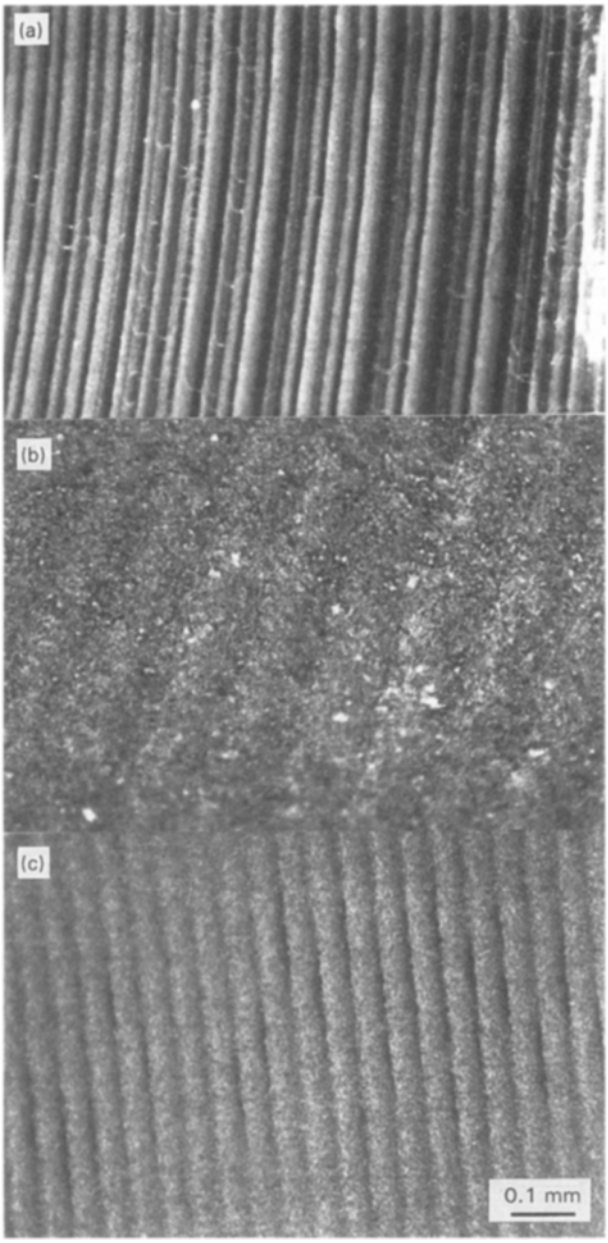

Figure 7 Optical micrographs of discontinuous growth bands at $\Delta K = 0.8$ MPa $m^{1/2}$ in (a) neat PETG, (b) 95/5 PETG/PD35, and (c) 95/5 PETG/PD20. Crack growth is from left to right.

the crack tip. According to the Dugdale plastic zone model [14]

$$r_y = \pi K_{max}^2 / 8\sigma_y \tag{2}$$

where r_y is the plastic zone size, σ_y is yield stress, and K_{max} is the maximum stress intensity factor. The effective yield stress can be determined by setting r_y equal to the DGB width and K_{max} equal to $\Delta K/(1 - R)$, where R equals K_{min}/K_{max}.

A plot of effective yield stress versus ΔK for both sets of blends and for neat PETG is shown in Fig. 9. (Data for blends containing 15 wt % modifiers are not plotted because the DG bands were extremely diffuse and difficult to identify unambiguously.) The tensile yield and craze stresses of neat PETG are highlighted in Fig. 9. The craze stress was determined using a blunt notch, three-point bend test described by Ishikawa *et al.* [15]. The effective yield stress of neat PETG is approximately equal to its craze stress, suggesting that fatigue crack propagation occurs by craze formation. The effective yield stress of each PETG/PD35 blend is fairly independent of ΔK and is approximately equal to the tensile yield stress shown in Fig. 1. The effective yield stress of each PETG/PD20 blend, on the other hand, increases slightly with increasing ΔK and approaches the craze stress of neat PETG. These results indicate that, although FCP rates in the two sets of blends are similar, shear yielding may dominate fatigue crack propagation in the PETG/PD35 blends and that crazing may dominate fatigue crack propagation in the PETG/PD20 blends. The prevalence of crazing in the PETG/PD20 blends may be due to the low IV of the PETG component. The particle size of PD20 may also play an important role; the smaller PD20 rubber particles may not be able to cavitate as readily as the larger PD35 rubber particles and relieve the triaxial stresses which promote crazing [16].

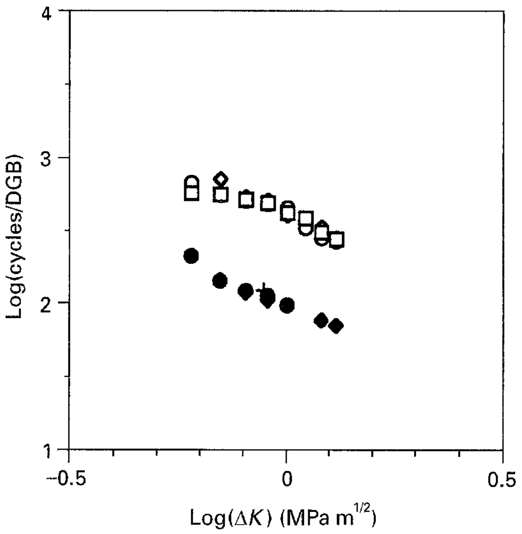

Figure 8 Log–log plot of cycles/DGB versus ΔK. Symbols are the same as in Figs 4–6.

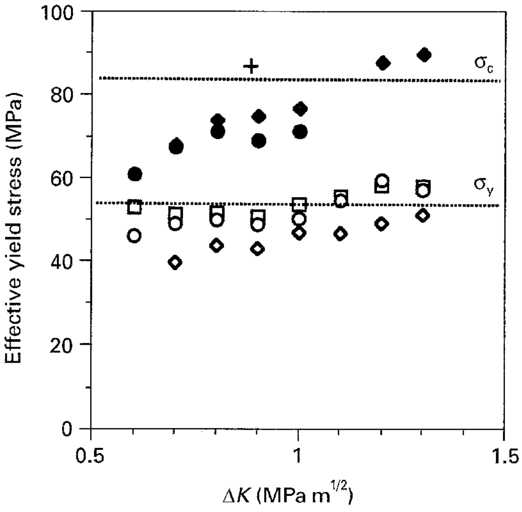

Figure 9 Effective yield stress of impact modified PETG blends. Symbols are the same as Figs 4–6.

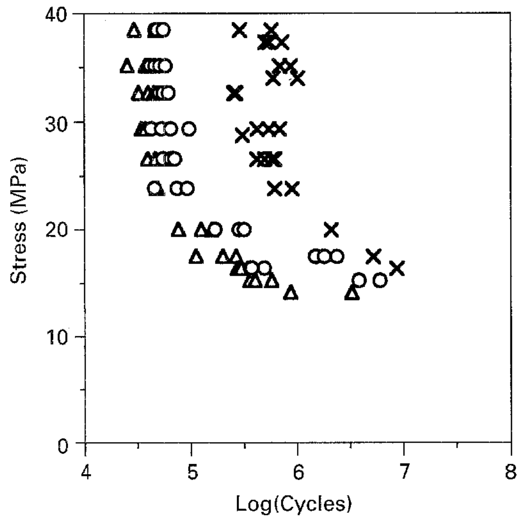

Figure 10 Plot of stress versus logarithm of number of cycles to failure for (×) neat PETG, and PETG/PD35 blends containing (○) 5%, and (Δ) 15% PD35.

The fatigue resistance of PETG/PD35 blends was also evaluated in flexural fatigue tests on unnotched specimens according to ASTM D671-90 [13]. This method measures the number of cycles needed to initiate a crack and to propagate the crack to failure. A plot of stress versus the logarithm of cycles to failure (also known as an S–N diagram) is shown in Fig. 10. The addition of PD35 dramatically reduces the number of cycles to failure at all stress levels. Because the FCP rate in PETG is lowered by adding an impact modifier, as discussed above, crack initiation must be facilitated by the modifier particles. Similar results were observed in unnotched fatigue tests on toughened PVC [17] and high-impact polystyrene [18].

4. Conclusion

The FCP rate at a given value of ΔK in PETG decreased by a factor of 4 with the addition of an impact modifier, if the inherent viscosity of the PETG remained constant. The FCP rate did not vary with modifier concentration and particle size. The value of ΔK at instability, however, increased with increasing modifier concentration. Furthermore, particle size appeared to affect the FCP mechanism: crazing was favoured in blends containing the smaller particles and shear yielding was favoured in blends containing the larger particles. In fatigue tests on unnotched specimens, neat PETG was more fatigue resistant than the impact-modified blends, suggesting that the modifier particles reduced the number of cycles required to initiate a crack.

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