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Mechanical properties of injection-moulded styrene maleic anhydride (SMA)

Part I: *Influence of weldline and reprocessing*

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This paper presents the results from the first part of a study on the influence of reprocessing and weldlines on the properties of styrene maleic anhydride (SMA) polymer. Specimens for this study were injection moulded and reprocessed up to five times. It was found that while mechanical properties such as strength and modulus in both tension and flexure tests were virtually independent of the number of reprocessing cycles, the energy to fracture decreased as a result of reprocessing. Fracture parameters such as fracture toughness and strain energy release rate also showed little variation with reprocessing; although at times a reduction in these parameters was obtained for the fifth cycle. We found that tensile strength, fracture energy and fracture toughness were all reduced substantially in the presence of the weldline. However, none of these properties showed any significant variation with the number of reprocessing cycles. © *1998 Chapman & Hall*

1. Introduction

In recent years the practice of recycling has been encouraged and promoted because of the increased awareness in environmental matters and the desire to save resources. This together with the relatively high cost of some polymers and some times the high levels of scrap material generated during manufacture makes this procedure both a viable and attractive proposition. Therefore, the subject of recycling of polymers and, in particular, its effect on mechanical properties has received some attention by several investigators [e.g. 1–4]. However, surprisingly, apart from studies by Chrysostomou and Hashemi on polycarbonate [4], there is little if any, information, regarding the effect of reprocessing on weldline properties of reprocessed materials. Since most injection-moulded components do contain a weldline of some form or another, it is important to consider the effect that reprocessing might have on the durability and fracture behaviour of the welded components.

In this paper, we study the influence of reprocessing by injection moulding on the mechanical properties of styrene maleic anhydride (SMA) material under tensile and flexural loadings. The fracture behaviour is also investigated under both types of loading using single edge notched specimens. A similar study is performed on specimens that contain a weldline. The aims of this study were first to investigate the effect of the presence of a weldline on mechanical properties of SMA material and second, to see if such properties are affected by the reprocessing of the material.

2. Materials

The styrene maleic anhydride (SMA 400) used in this study was Stapron S supplied by DSM. The material was dried prior to all processing cycles for 3 h at 90 °C, as recommended by the manufacturer.

3. Mouldings

Two types of specimens were injection moulded:

(i) *Tensile bars*: dumbbell shaped specimens of nominal dimensions 1.7 × 12.5 × 125 mm (thickness, width, length) were produced on a Negri Bossi NB60 with the melt temperature set at 230 °C and the mould temperature set at 80 °C. Injection speeds reached rpm while the pressure were held at 71 GPa. The mould used consisted of two cavities, a single feed and a double-feed cavity. In the latter, a weldline is formed as two opposing melt fronts meet at the centre.

(ii) *Flexural bars*: flexural bars were produced on a Klockner Ferromatic injection moulding machine using an edge gated cavity of nominal dimensions 4 × 10 × 120 mm (thickness, width, length). The processing temperature was set at 230 °C and the mould temperature at 80 °C with a pressure of 75 MPa.

4. Reprocessings

The material was received in the form of granules and was at first injection moulded to produce the aforementioned test specimens. These specimens are referred to in the following text as virgin or zero cycle. After testing the virgin test pieces, they were then granulated on a Blackfriars 2000 granulator and remoulded (reprocessed) again to produce the first recycled test pieces. The regrinding and remoulding procedures were carried out five times, maintaining the processing conditions as closely as possible to those which were used for the virgin cycle. Each subsequent cycle after the zero cycle, was referred to as, first cycle, second cycle, ... and fifth cycle.

5. Results and discussion

5.1. Infrared (i.r.) analyses

A Perkin Elmer 1600 Fourier transform infrared (FTIR) spectrophotometer was used to perform infrared analysis on the material. Samples from each cycle under review (0, 1st, 3rd and 5th) were obtained by rubbing the relevant moulding across an abrasive disc, so obtaining particles suitable for conducting the test. Each disc was placed under an infrared beam and the resulting spectrograph was printed. Fig. 1 shows typical FTIR traces for the virgin and the reprocessed materials. Evidently, there are no changes in the spectra; thus indicating that there is no change in the intrinsic chemical structure of the SMA polymer on repeated reprocessing.

5.2. Melt flow index (MFI)

The melt flow index of SMA was measured after each reprocessing cycle using a Davenport rheometer. Measurements were carried out at a temperature of 220 °C and with a 10 kg load. It was noted that after each reprocessing cycle SMA progressively darkened.

Fig. 2 presents values of MFI for the virgin and the reprocessed materials, where each point represents an average value taken from five measurements (standard deviations about the mean values are given in parenthesis). As can be seen, the average MFI value for the virgin material is about 2.65 g/10 min compared to that of 2.85 g/10 min obtained for the reprocessed materials. Some degree of discoloration was also observed as a result of reprocessing. These observations suggest, that some form of degradation occurred during the reprocessing of the SMA material. An increase of 7% in the MFI value of the reprocessed materials led us to believe that some reduction in polymeric chain lengths has taken place during the reprocessing of the materials.

5.3. Dynamic mechanical analysis (DMA)

DMA test were performed on a Perkin Elmer 7 series using a three-point bend configuration. Test specimens of dimensions were cut from the dumbbell specimens and tested at a frequency of 1 Hz, dynamic force of 600 mN and a static force of 800 mN. The temperature range over which testing was conducted was between 30–150 °C using increments of 5 °C min^{-1}.

Fig. 3 shows typical traces of storage modulus and tan δ for the virgin and the reprocessed materials. Results obtained from these tests indicated that there is no significant variation in these quantities with the number of reprocessing cycles. The average storage modulus for the virgin material was 2.0 ± 0.07 GPa compared with that of 2.12 ± 0.11 GPa obtained for the reprocessed materials. It can also be deduced from

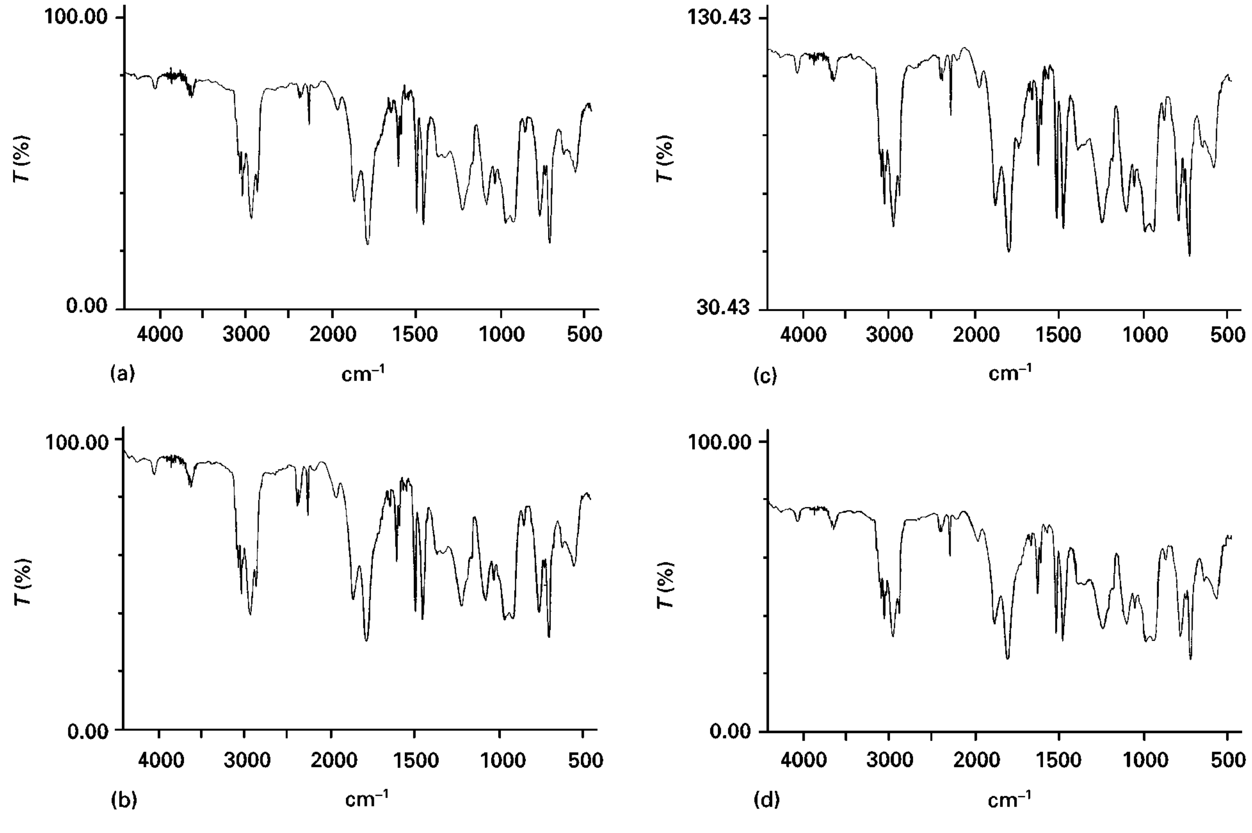

Figure 1 FTIR traces. (a) Virgin; (b) 1st cycle; (c) 3rd cycle; (d) 5th cycle.

the traces that the glass transition temperature, T_g, of SMA is not affected by repeated reprocessing. T_g was found to be within the temperature range of 139–142 °C over the entire reprocessing cycles.

5.4. Tensile tests

Tensile tests were carried out on dumbbell shaped specimens with and without weldlines at room temperature in an Instron testing machine at a crosshead speed of 5 mm min^{-1}. Fig. 4 shows typical load–displacement diagrams of the virgin and the material that had been reprocessed five times, for both weld and non-weld specimens. The load–displacement diagram of the two non-weld specimens exhibits a clear yield point. The failure of non-weld specimens can be described as ductile in so far as the point of fracture occurs after the yield point. It is also apparent, that although reprocessing does not affect the general behaviour of the load–displacement diagram, it nevertheless affects the extent to which the material is deformed or extended.

As regards weld specimens, it is evident from Fig. 4, that the load–displacement diagram for this type of specimen is almost linear up to the point of failure.

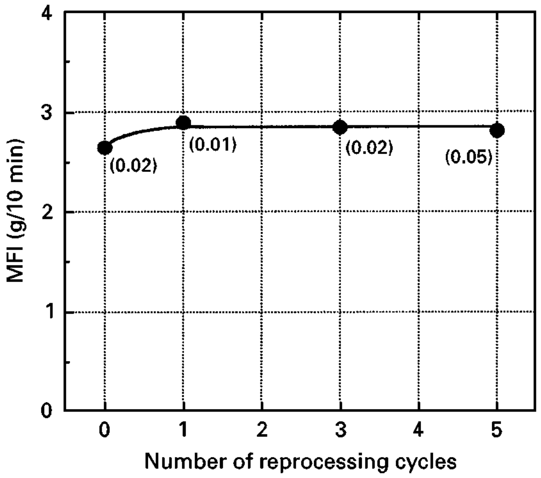

Figure 2 Melt flow index (MFI) versus the number of reprocessing cycles.

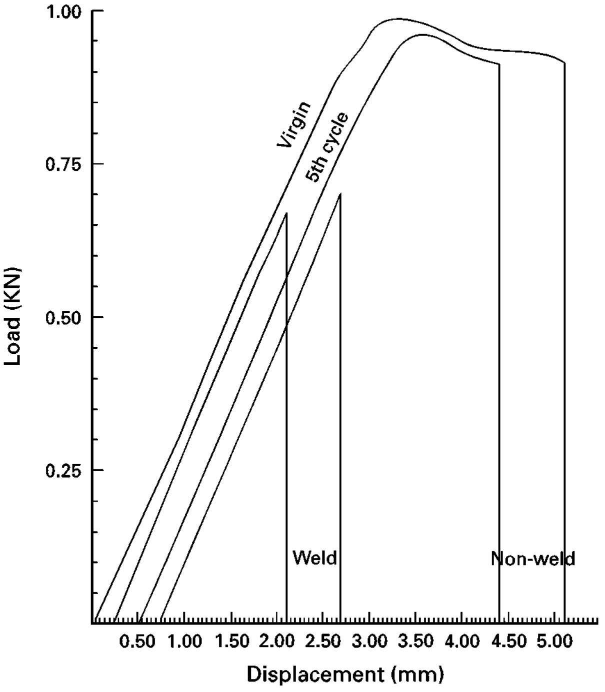

Figure 4 Tensile load –displacement diagrams for the weld and non-weld specimens (virgin and the 5th cycle).

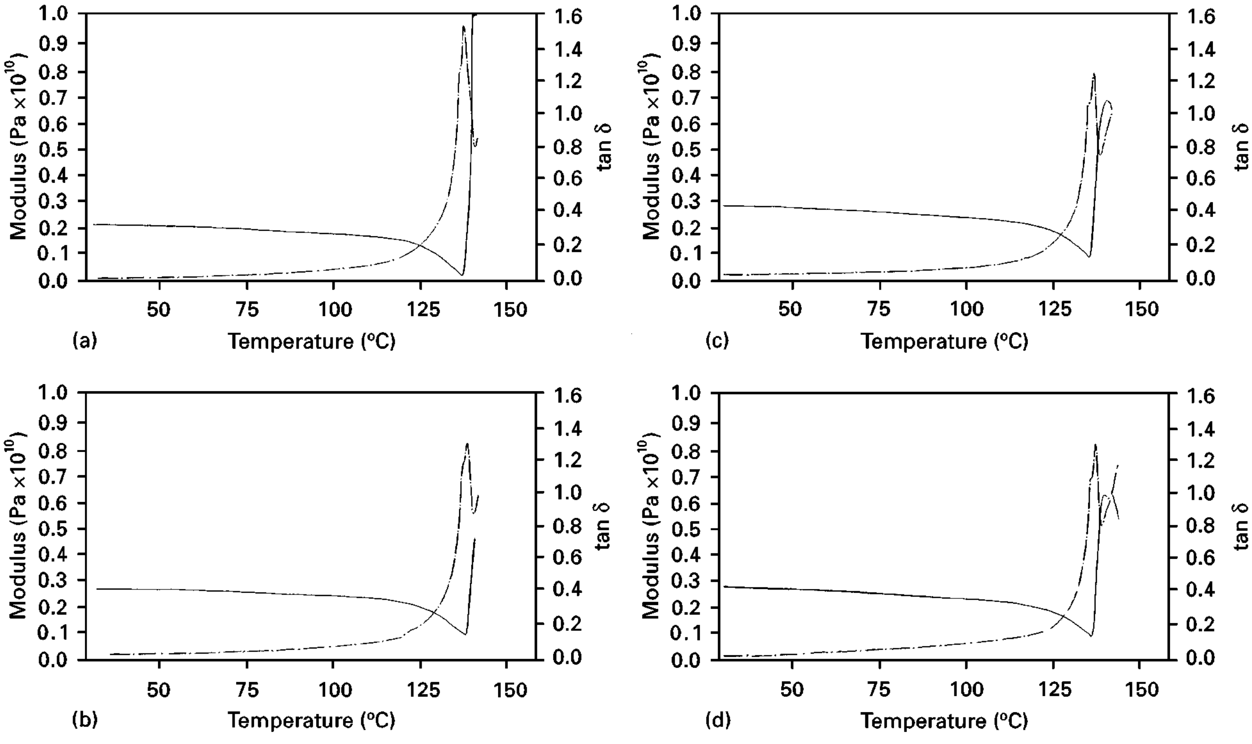

Figure 3 DMA traces. (a) Virgin; (b) 1st cycle; (c) 3rd cycle; (d) 5th cycle.

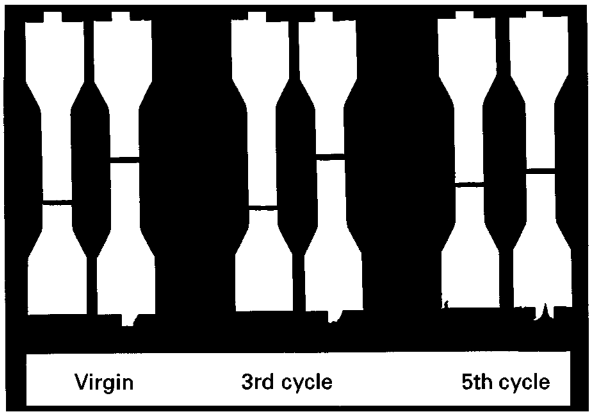

Figure 5 Typical tensile test specimens.

The failure of the weld specimens can be described as brittle so far as no yeild point was detected. Notice that, the reprocessing of the material has no effect upon the general behaviour of the load–displacement diagram or the extent to which the specimen is deformed.

The difference in fracture behaviour of weld and non-weld specimens is further highlighted in Fig. 5, where the broken specimens at each reprocessing cycle are compared. As can be seen, while non-weld specimens show some degree of stress whitening, which is indicative of their ductility, weld specimens show no sign of stress whitening.

Tensile strength of both weld and non-weld specimens as a function of the number of reprocessing cycles is shown in Fig. 6a. As can be seen, there is little variation in this quantity with the number of reprocessing cycles for both weld and non-weld specimens. The percentage change over the entire range of reprocessing cycles is no more than 6% for each type of test specimens which is within the limits of experimental error.

Results obtained from the tensile tests on both weld and non-weld specimens are plotted in Fig. 7a–c as a function of the number of reprocessing cycles. The averaged value for the non-weld specimens is identified by a filled circle and that of weld specimens by an open circle. Standard deviation associated with each averaged value is given in the parentheses.

The effect of weldline on tensile strength is quite striking. As illustrated in Fig. 6, tensile strength is greatly lowered in the presence of the weldline: the value of tensile strength for non-weld specimens is about 1.5 times greater than that for weld specimens.

Regarding tensile modulus and its variation with number of reprocessing cycles, as shown in Fig. 6(b) for both weld and non-weld specimens, one can state with a reasonable degree of confidence, that there is no significant variation in this quantity with the number of reprocessing cycles. Moreover, it is evident also, that tensile modulus is not affected by the weldline in the specimen. This suggests that at low strain levels where behaviour of SMA is almost linearly elastic, the presence of the weldline has no major influence upon the deformation of SMA. This is further illustrated by the load–displacement diagrams in Fig. 4.

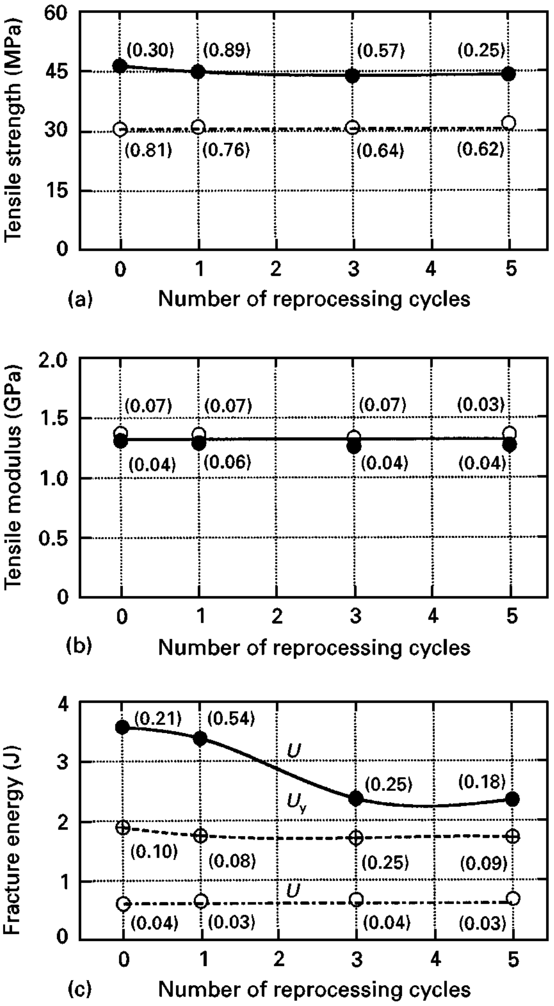

Figure 6 Tensile properties as a function of the number of reprocessing cycles for weld and non-weld specimens.

The quantity associated with non-weld specimens that shows a considerable variation with the number of reprocessing cycles is fracture energy (the total area under the load–displacement diagram). According to Fig. 6c as the number of reprocessing cycles increases, fracture energy decreases. A drop in fracture energy of about 30% was incurred as a result of reprocessing. It is worth noting that, as energy to yield (U_y) shows very little variation with number of reprocessing cycles, the decrease in fracture energy must be due to the reduction in ductility which is brought about by repeated reprocessing of the material. Moreover, a significant drop in fracture energy is also incurred in the presence of the weldline, although in this case, fracture energy shows no significant variation with the number of reprocessing cycles. The negligible variation in fracture energy of weld specimens with number of reprocessing cycles is a reflection of the brittle nature of these specimens. The percentage drop in fracture energy for the virgin material due to the presence of the weldline is 83% compared to that of 71% for the reprocessed materials (3rd and 5th cycles).

5.5. Flexural tests

The three-point flexural modulus and strength as a function of reprocessing cycles were determined by

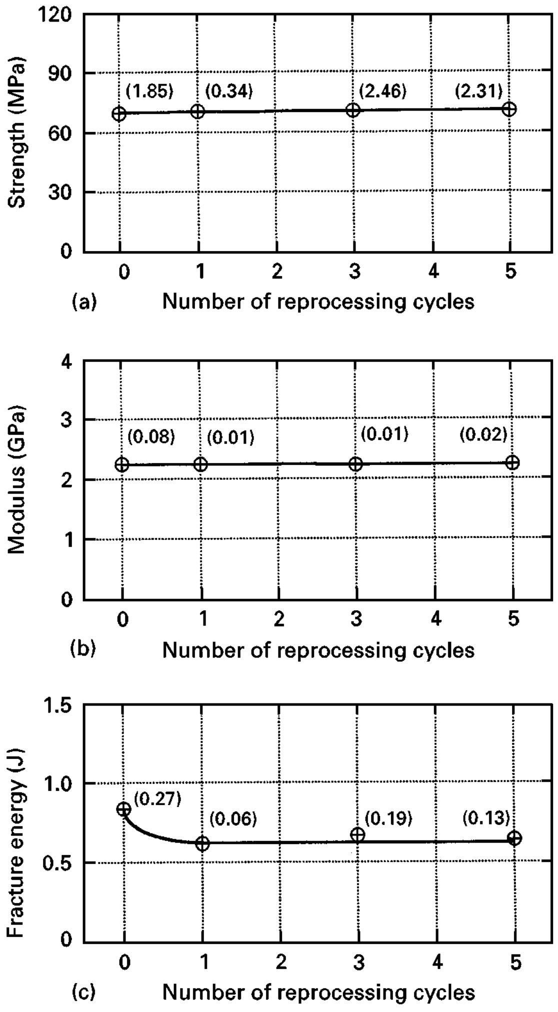

Figure 7 Flexural properties as a function of the number of reprocessing cycles.

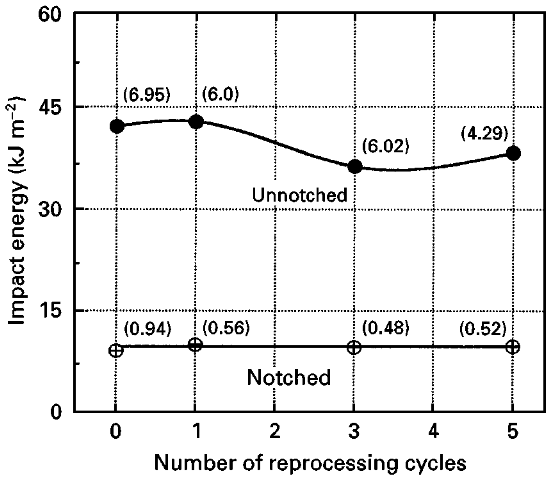

Figure 8 Notched and unnotched impact strengths versus the number of reprocessing cycles.

testing the flexural bars at a crosshead speed of 5 mm min^{-1} with a span of 64 mm (i.e. span to depth ratio of 16 : 1). The load–displacement diagrams obtained from these tests were linear at first but became non-linear as the maximum load was reached (all the specimens broke soon after the maximum load). The quantities measured from the load–displacement diagrams were: flexural strength calculated using the maximum load, flexural modulus, E, calculated using the initial slope of the diagram and the energy to fracture, U, determined from the total area under the diagram.

Results obtained from the flexural tests are presented in Fig. 7a–c where it can be seen that apart from fracture energy which shows a reduction of about 27% as a result of repeated reprocessing, there is no significant variation in other quantities with the number of reprocessing cycles.

It is worth noting that the strength and modulus values obtained from the flexural tests were higher than those obtained via tensile tests. These differences we believe are artificial, because they arise in one of two ways. First, tensile modulus is measured using grip displacement rather than by external means. Second, flexural strength is evaluated using linear elastic equation even though the deformation of test pieces did not warrant this approach. It should be realized that the ratio of two (flexural strength: tensile strength) is close to 1.5; which is the ratio expected when cross-section of the flexural bar is yielded prior to attainment of the maximum load.

5.6. Impact tests

The notched and unnotched impact tests were performed on flexural bars using a Charpy impact machine. Specimens were notched to an a/D ratio of 0.3 using a V-shaped cutter with tip radius of 0.25 mm. Specimens were then impacted in a three-point bend configuration with a span of 40 mm (this gives a span to depth ratio of 4 : 1) at a pendulum speed of 3 m s^{-1}. Impact energy per unit area of the unnotched section was then calculated for each specimen and plotted as a function of the number of the reprocessing cycles as shown in Fig. 8, where each data point represents an average value of at least five measurements. As can be seen, the unnotched impact strength decreases slightly from an average value of about 42.50 kJ m^{-2} for the virgin material to that of about 37.70 kJ m^{-2} for the material that has been reprocessed five times. This difference is not very significant bearing in mind that the percentage change over the entire reprocessing cycles is not more than 12%, which is well within the range of scatter associated with each average value.

As for notched specimens, impact energy also showed very little variation with number of reprocessing cycles. The difference in values across the entire processing cycle is no more than 10% which is well within the limits of experimental error.

5.7. Tensile testing of notched bars

Fracture testing of the notched bars was performed on single-edge notched tension (SENT) specimens. Rectangular coupons of dimensions 1.7 × 12.5 × 70 mm (thickness, depth, length) were cut from the parallel portion of the dumbbell specimens and subsequently edge notched to various a/D ratios (a = crack length, D = specimen depth) ranging from 0.1–0.6 using a razor blade. In the case of specimens with a weldline, care was taken to ensure that the initial notch was inside the weldline. It is worth mentioning at this point that in several specimens the initial notch was seen to be just outside the weldline at the interface between the weld and unweld part of the specimen.

After notching, each specimen was loaded in tension to complete failure using pneumatic clamps with a gauge length, Z, of 50 mm. All tests were performed in an Instron testing machine at a constant crosshead displacement rate of $5\,\mathrm{mm\,min^{-1}}$.

In all cases, the initial notch propagated perpendicular to the direction of the applied stress. The manner in which both weld and non-weld specimens were fractured was typical of brittle failure as reflected by the triangular nature of their load–displacement diagrams, examples of which are shown in Fig. 9a. The nature of these traces and the way in which the specimens were fractured was not affected by the number of reprocessing cycles.

Using the maximum load on the load–displacement diagram, fracture stress, σ_f for each specimen was calculated. In the majority of test specimens, except those with shallow notches, stress at fracture was found to be considerably smaller than that required for net-section to yield. Consequently, the concept of linear elastic fracture mechanics (LEFM) was used to determine the fracture toughness, K_{Ic}, of SMA material under the conditions used here.

Using the fracture stress and the initial length of the crack, fracture toughness, K_{Ic}, was calculated from the well known linear elastic fracture mechanics (LEFM) relationship [5]

$$K_{Ic} = \sigma_f Y (a)^{1/2} \tag{1}$$

In accordance with Equation 1, K_{Ic} of the SMA material at each reprocessing cycle (for both weld and non-weld specimens) was determined from the slope of the line σ_f versus $1/Y(a)^{1/2}$ as shown in Figs 10 and 11, where Y is the finite width correction factor defined by [6]

$$Y = \frac{5(\pi)^{1/2}}{[20 - 13(a/D) - 7(a/D)^2]^{1/2}} \tag{2}$$

It may be deduced from Fig. 10 that for non-weld specimens, the slopes of the plots of fracture stress versus $1/Y(a)^{1/2}$ are identical for the first three cycles, giving an average fracture toughness value of $2.57\,\mathrm{MPa\,m^{1/2}}$. However, for the material that has been reprocessed five times there appears to be a significant reduction in fracture toughness as reflected by the 95% confidence limits associated with each value.

As regards weld specimens, it may be similarly deduced from Fig. 11 that the slopes (fracture toughness) show no significant variation with number of reprocessing cycles. However, in this case the average value for fracture toughness is about $1.64\,\mathrm{MPa\,m^{1/2}}$ compared to $2.57\,\mathrm{MPa\,m^{1/2}}$ obtained from the non-weld specimens. This represents approximately 35% difference which may be attributed to the introduction of weldlines in the specimens. It should be noted that a difference of the same order of magnitude was reflected in tensile strength values. It is worth noting also, that the scatter associated with weld specimens is somewhat higher than that for non-weld specimens. As mentioned earlier, considerable care was taken to ensure that the initial notch was placed inside the weldline. However, as the weldline in SMA material is not easily identifiable (as indicated in Fig. 5), this led at

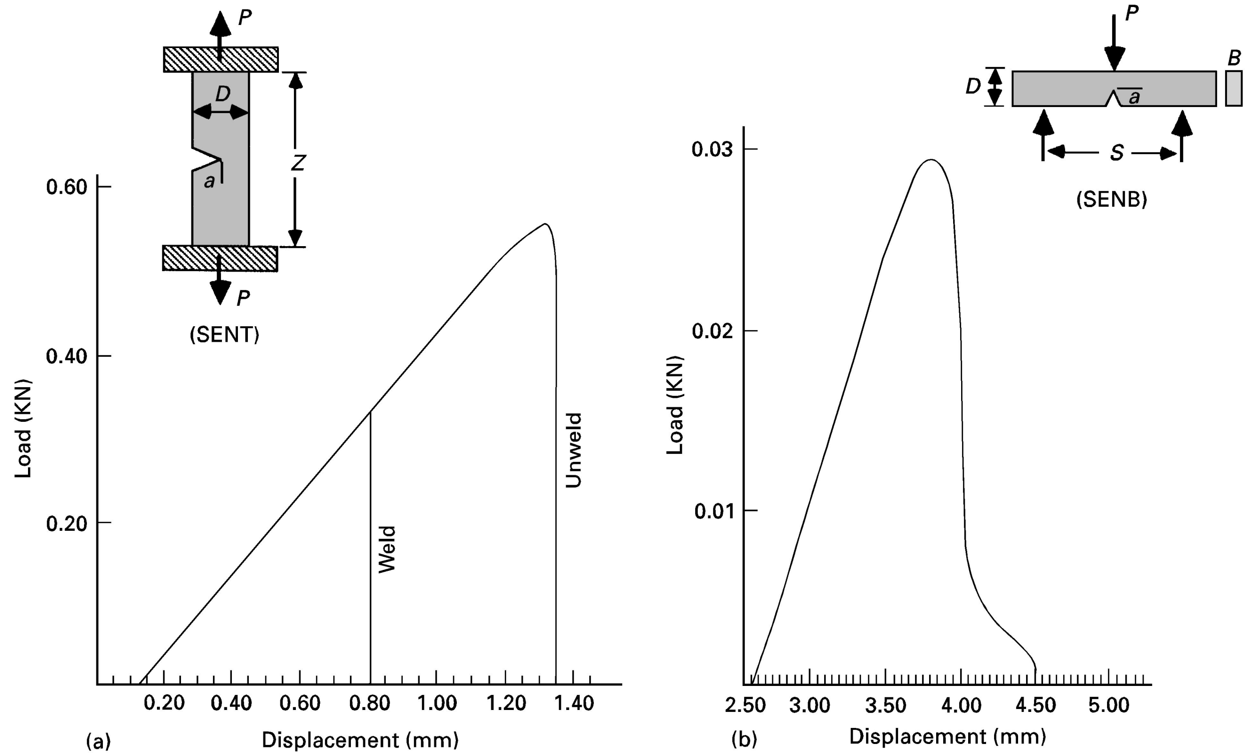

Figure 9 Typical (a) SENT and (b) SENB load–displacement diagrams.

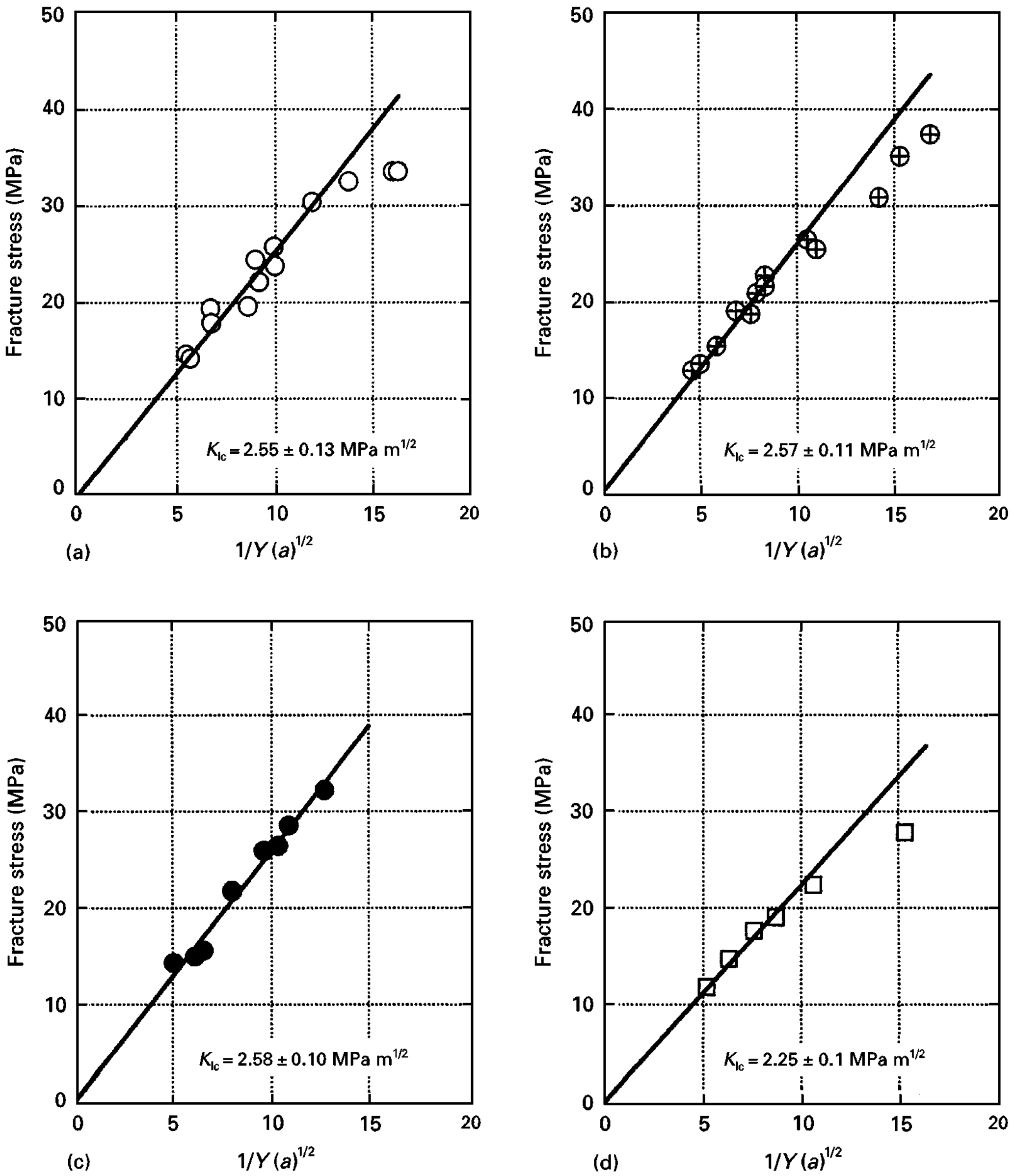

Figure 10 Plots of fracture stress versus $1/Y\ (a)^{1/2}$ for non-weld SENT specimens at various reprocessing cycles. (a) Virgin; (b) 1st cycle; (c) 3rd cycle; (d) 5th cycle.

times to the initial notch being accidentally inserted at close proximity to the weldline rather than inside it. Owing to the differences in measured fracture stresses for the two cases the plots of fracture stress versus $1/Y(a)^{1/2}$ exhibited greater degree of scatter. This is reflected in the higher confidence limits for weld compared to non-weld specimens. Further information regarding the toughness of the material was ascertained through the measurements of the area under the load–displacement diagrams (fracture energy). These values are plotted per unit thickness as a function of crack length in Fig. 12a, b for the weld and non-weld specimens, respectively. As expected, fracture energy decreases as crack length increases but no significant change is incurred due to reprocessing of the material. A considerable reduction in fracture energy was obtained due to the presence of the weldline. Moreover, it was found that when the initial notch resided within the weldline a lower fracture energy was obtained in contrast to when the notch resided just outside the weldline. This difference is indicated in Fig. 12b in which the solid curve represents the latter situation and the broken curve represents the former.

5.8. Flexural testing of notched bars

The fracture testing of the notched flexural bars was performed on single-edge notched bend (SENB) specimens with dimensions of $4 \times 10 \times 120$ mm (thickness, depth, length). Specimens were edge notched to various a/D ratios ranging from 0.1–0.7, as described earlier. Specimens were then tested to complete failure in an Instron testing machine at a constant crosshead speed of 5 mm min^{-1} in a three-point bend configuration with a span of 40 mm (i.e. span-to-depth ratio of 4 : 1). A typical load–displacement diagram is shown in Fig. 9b, where it can be seen that at maximum load the crack has propagated unstably through the specimen at which point tearing of the skin layer was initiated.

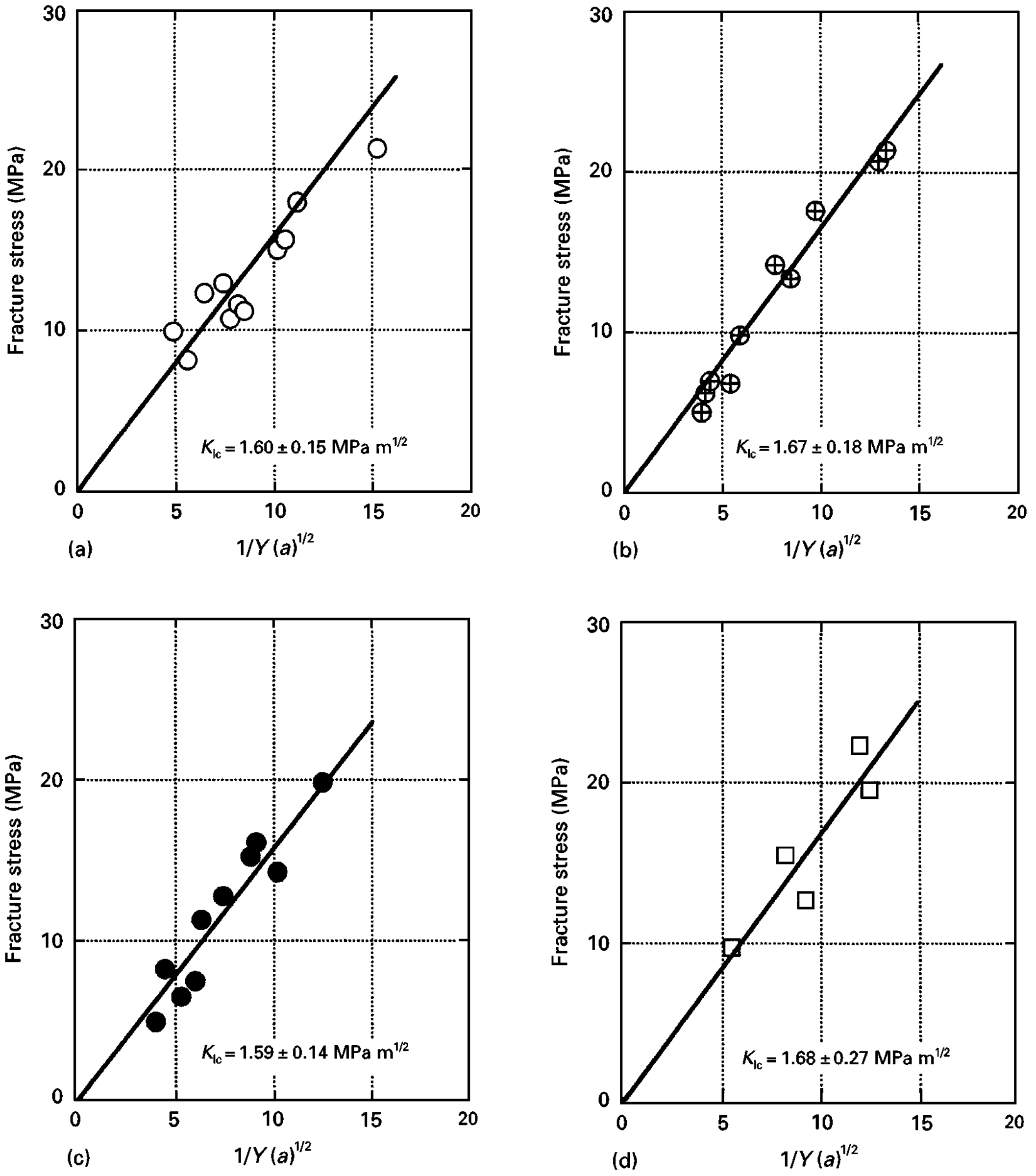

Figure 11 Plots of fracture stress versus $1/Y\ (a)^{1/2}$ for weld SENT specimens at various reprocessing cycles, as in Fig. 10.

Plots of fracture stress calculated at maximum load versus $1/Y(a)^{1/2}$ for the virgin and the reprocessed materials are shown in Fig. 13 (Y function for this geometry is given in ref [5]). It can be deduced from the slopes of these plots that fracture toughness (K_{Ic}) is not affected by the reprocessing of the material. The average K_{Ic} value for SENB geometry is $1.98\,\mathrm{MPa\,m^{1/2}}$ compared to that of $2.57\,\mathrm{MPa\,m^{1/2}}$ obtained by way of SENT specimens. This difference in fracture toughness values is attributed to the fact that plane strain conditions are not achieved at the crack tip, particularly in SENT specimens. By invoking the minimum specimen thickness criterion of [5]

$$B_{\mathrm{c}} = 2.5\left(\frac{K_{\mathrm{Ic}}}{\sigma_{\mathrm{y}}}\right)^2 \tag{3}$$

for valid plane strain fracture toughness and using the toughness value of $K_{\mathrm{Ic}} = 1.98\,\mathrm{MPa\,m^{1/2}}$ and the tensile yield stress value of $\sigma_{\mathrm{y}} = 44.87\,\mathrm{MPa}$, gives B_{c} of 4.9 mm. According to this value, while the state of stress in SENB specimens is one of near plane strain, that of SENT specimens is clearly of plane stress.

Values of fracture energy, U, up to the maximum load per unit thickness as a function of a/D are plotted in Fig. 14. It can be seen that variation is fairly linear for a/D ratios greater than 0.2. Above this ratio and because of the higher degree of scatter present, the slopes of the lines may not be significantly affected by the number of reprocessing cycles. Using the slopes of the lines, strain energy release, G_{Ic}, at each cycle was determined from the relationship [5]

$$G_{\mathrm{Ic}} = -\frac{1}{B}\frac{\mathrm{d}U}{\mathrm{d}a} \tag{4}$$

It can be deduced from the values given in Fig. 14, that G_{Ic} is not affected significantly by the number

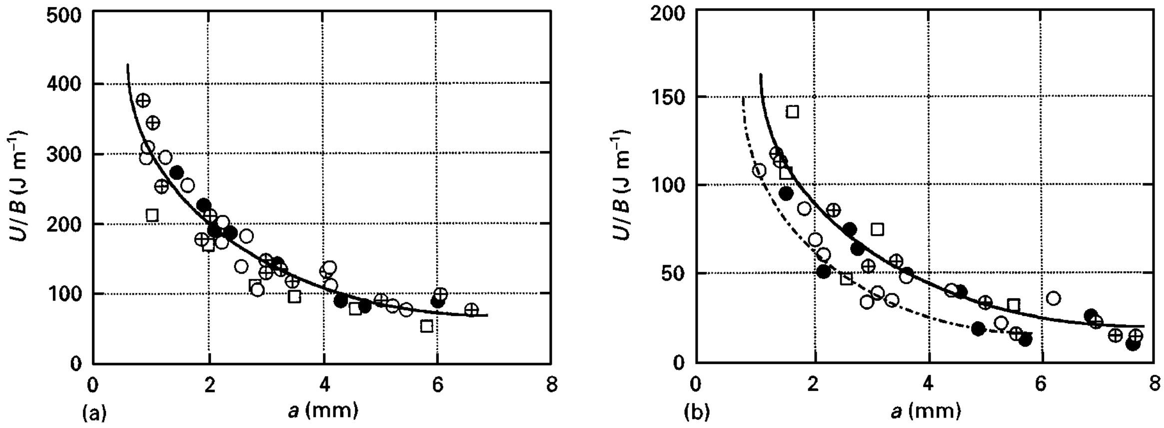

Figure 12 Work of fracture per unit thickness as a function of a/D for SENT specimens. (a) Non-weld; (b) weld. (○) Virgin; (⊕) 1st cycle; (●) 3rd cycle; (□) 5th cycle.

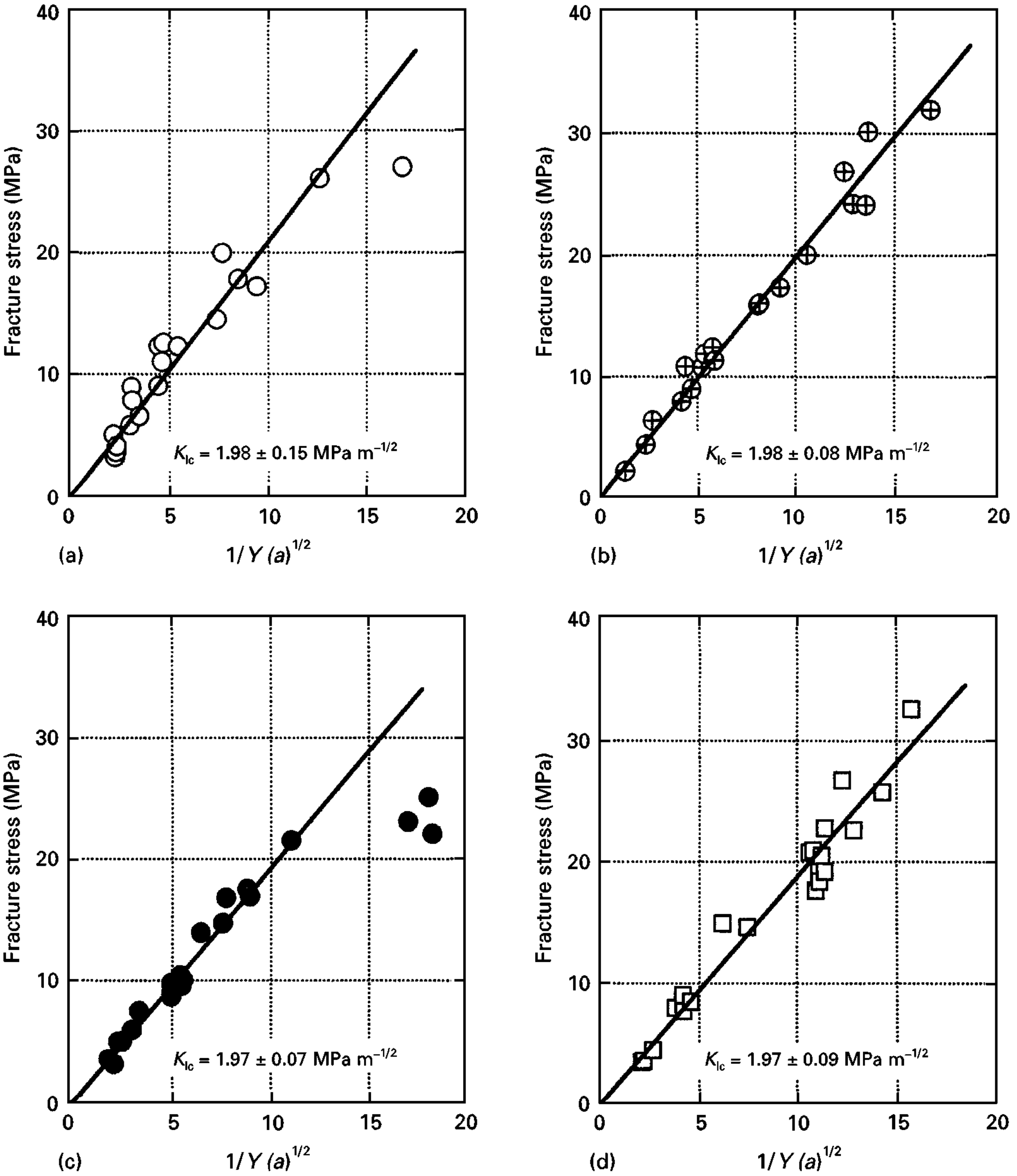

Figure 13 Plots of fracture stress versus $1/Y(a)^{1/2}$ for SENB specimens at various reprocessing cycles. (a) Virgin; (b) 1st cycle; (c) 3rd cycle; (d) 5th cycle.

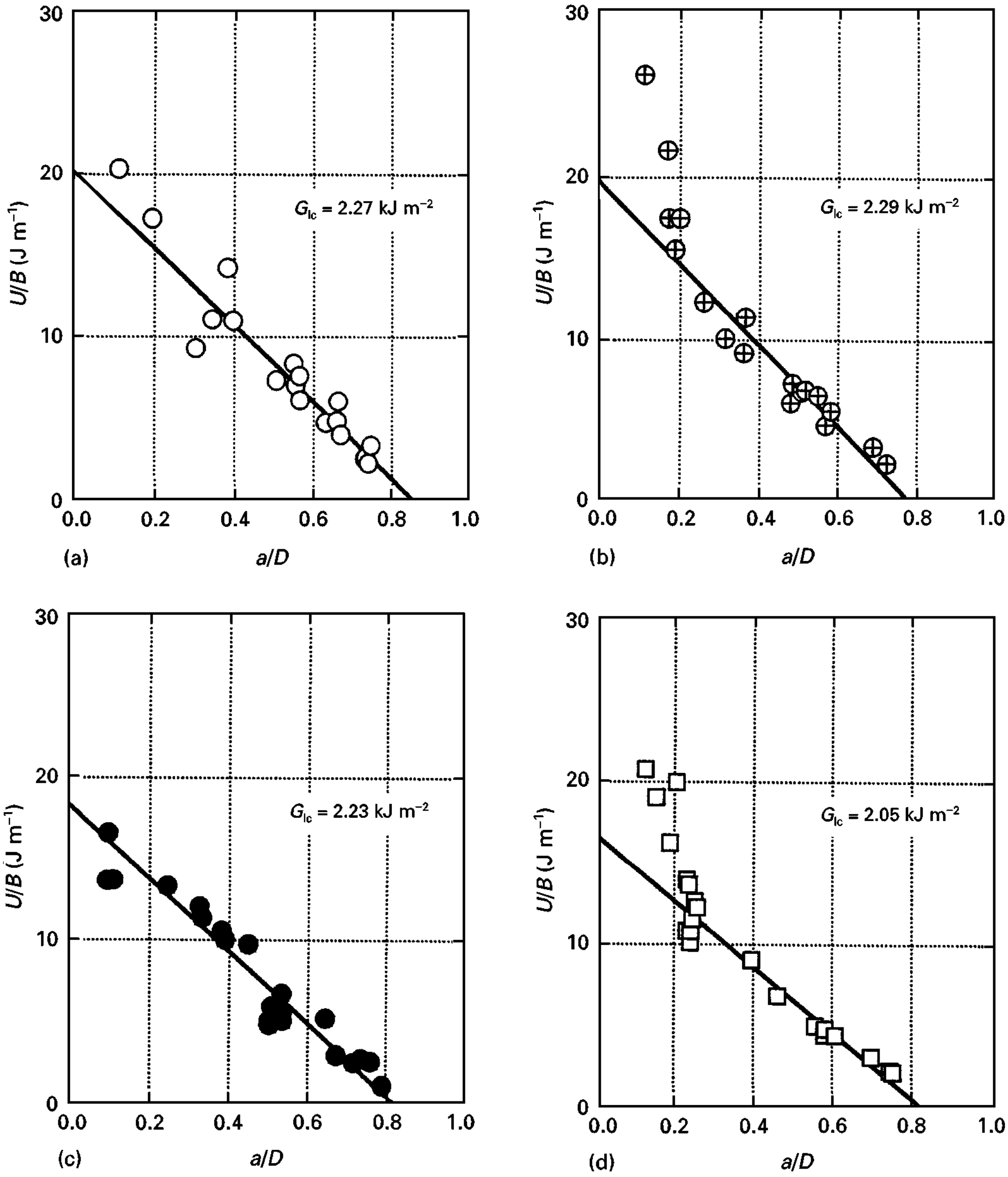

Figure 14 Plots of work of fracture per unit thickness as a function of a/D for SENB specimens. (a) Virgin; (b) 1st cycle; (c) 3rd cycle; (d) 5th cycle.

of reprocessing cycles, having an average value of $2.21 \pm 0.11\,\mathrm{kJ\,m^{-2}}$. Using the relationship

$$K_{Ic} = (EG_{Ic})^{1/2} \qquad (5)$$

with flexural modulus, E, of 2.24 GPa and G_{Ic} of 2.21, one obtains a K_{Ic} value of $2.23\,\mathrm{MPa\,mm^{1/2}}$. This value agrees reasonably well with the value of $1.98\,\mathrm{MPa\,m^{1/2}}$ obtained directly from the plots of the fracture stress versus $1/Y(a)^{1/2}$ (see Fig. 13).

6. Conclusions

This study has revealed that:

1. Tensile strength and modulus are relatively insensitive to the number of reprocessing cycles.
2. Flexural strength and modulus are relatively insensitive to the number of reprocessing cycles.
3. Fracture energy of the virgin material is higher than that of the reprocessed material.
4. Dynamic properties such as storage modulus and tan δ are insensitive to the number of reprocessing cycles.
5. Charpy impact strengths are not affected significantly by repeated reprocessing.
6. Fracture toughness and strain energy release rate are not affected significantly by reprocessing of the material.
7. Presence of the weldline reduces tensile strength and fracture energy but does not affect tensile modulus.
8. Presence of the weldline reduces fracture toughness.
9. Weldline properties are insensitive to the number of reprocessing cycles.

Acknowledgements

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References

1. J. I. EGUIAZABAL and J. NAZABAL, *Eur. Polym.* **14** (1989) 891.
2. K. B. ABBAS , *Polym. Eng. Sci.* **20** (1980) 376.
3. A CHRYSOSTOMOU and S. HASHEMI, *J. Mater. Sci.* **31** (1996) 1183.
4. *Idem., ibid.* **31** (1996) 5573.
5. W. F. BROWN and J. E. SRAWLEY, "Plane strain crack toughness testing of high strength metallic materials", ASTM STP 410 (American Society for Testing and Materials, Philadelphia, 1987) p. 810.
6. D. O. HARRIS, *J. Bas. Eng.* **49** (1967) 89.

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and accepted 23 October 1997