

is slightly deleterious.

Their data can, however, be interpreted in an alternative manner. If fibre bunching were to have no effect on toughness we would have  $W \propto n$ . It can be seen, however, that for  $n \geq 3$  the effect of  $n$  on work-to-fracture is  $W \propto 4/3 n$ , indicating a beneficial effect due to fibre bunching but with a threshold value of three fibres per group before this beneficial effect begins. Calculations from data in the paper show that the fibre volume fraction for this threshold is only 0.2% and the threshold phenomenon can, therefore, be ignored for practical composites.

In summary, therefore, the data of Harris and Ankara tend to support the existing suggestions that fibre bunching can increase the fracture toughness of brittle fibre–brittle matrix com-

posites as well as of brittle fibre–ductile matrix composites.

## References

1. R. E. COOPER, *J. Mech. Phys. Solids* **18** (1970) 179.
2. *Idem*, British Patent no. 1 289 823 (1972).
3. G. A. COOPER and A. KELLY, *J. Mech. Phys. Solids* **15** (1967) 279.
4. B. HARRIS and A. O. ANKARA, *Proc. Roy. Soc. Lond. A* **359** (1978) 229.

Received 31 July and accepted  
3 November 1978.

R. E. COOPER  
*Metallurgy Division,*  
*AWRE,*  
*Aldermaston,*  
*Berks, UK*

## A fracture energy spectrometer for polymers

This letter describes a simple technique for measuring the fracture energy spectrum of a polymer by slowly tearing a strip of the material while continually increasing its temperature. Plotting the tear force against the temperature yields the fracture energy spectrum of the polymer. Both experimental and theoretical studies demonstrate that this spectrum reflects the mechanical relaxation behaviour of the material.

The experimental system closely follows the trouser leg geometry used to study crack growth in rubber by Rivlin and Thomas [1]. In this configuration, a polymer strip is torn at constant speed on a testing machine and the tearing force is measured. Thomas and his colleagues later extended the method to look at rubbers over wide ranges of rate and temperature, allowing a spectrum of tear energy to be plotted [2].

Our only modification of this apparatus, shown in Fig. 1, was the incorporation of deep fissures cut along the sides of the polymer sample (compression moulded, 1 mm thick, 20 mm wide) by means of a tool containing two steel blades set 0.22 mm apart. These cuts were necessary for three reasons:

(1) to allow tough, cold-drawing polymers to be tested; low-density polyethylene, for example, will

not tear unless notched in this way;

(2) to guide the crack along the desired path; the tear will only go straight when deep cuts are made;

(3) to allow adjustment of the tearing force to suit the bending of the legs of the specimen; with brittle materials, such as polyvinylchloride at low temperatures, deeper cuts are necessary to prevent excessive bending and consequent cracking of the legs.

This tearing method has a number of fundamental advantages when compared with the conventional tensile or impact tests which have previously been used, not altogether successfully, in attempts to relate ultimate properties to relaxation behaviour [3–6]. In the first place, the tearing test is continuous rather than catastrophic so that a single sample can be used over the complete temperature range. This avoids the inaccuracies of different samples for each data point and the inconvenience of inserting a multiplicity of specimens into the controlled temperature cabinet. Secondly, the crack speed is held closely at a constant value in the tearing geometry. This factor is important because fracture energy is often a strong function of crack speed, and tests which allow speed to vary (such as impact and tensile tests) usually give irreproducible results. Last, but not least, the theory of the tear test is much simpler than that of tensile or flex

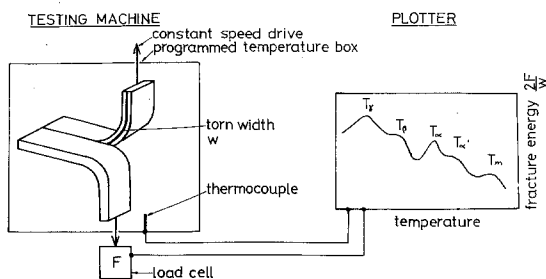


Figure 1 The fracture energy spectrometer.

cracking. This theoretical simplicity allows a proper understanding of fracture processes in a lossy material.

The energy theory of rubber tearing [1] was an impressive extension of Rivlin's approach to peeling paint films [7] and a worthy companion to the arguments of Griffith [8] and Obreimoff [9] concerning the fracture of ceramics. Drawing on the same parallel between tearing and peeling used by Rivlin, it is now possible to employ recent developments of peeling theory [10–13] in demonstrating that tearing force is influenced by viscoelastic displacements.

By contrast, during elastic tearing, an insignificant change in elastic energy arises as tearing progresses a distance  $\delta x$  (Fig. 2a). Thus, the energy  $2F\delta x$  expended by the tearing forces must equal the surface energy  $Rw\delta x$  created by the crack, where  $R$  is the fracture surface energy; the energy required to crack unit area of material. Therefore,

$$F_{\text{elastic}} = \frac{Rw}{2}, \quad (1)$$

showing that tearing force directly measures the fracture energy of the elastic material, independent of elastic modulus.

However, the process is not entirely independent of elastic modulus because, if the modulus changes during the tearing event, then the shape of the bent legs of the trouser will alter. If the elastic modulus relaxes linearly from  $E_1$  to  $E_2$ , then the legs will droop (Fig. 2b) and the tearing force must rise in consequence to around [13]

$$F_{\text{viscoelastic}} = \frac{E_1}{E_2} \left( \frac{Rw}{2} \right). \quad (2)$$

This equation, analysed in more detail elsewhere [14], shows that the fracture energy of a material appears to be increased to  $RE_1/E_2$  by a visco-

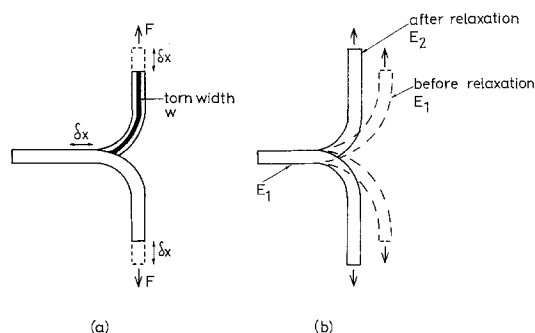


Figure 2 (a) Elastic tearing; (b) viscoelastic tearing showing droop of the trouser legs after relaxation of modulus from  $E_1$  to  $E_2$ .

elastic relaxation, although the intrinsic fracture property  $R$  might remain unchanged.

The results were intended to verify this equation in two ways, first by means of a model experiment in which an artificial relaxation was used to increase the tear force, and secondly, by showing that the tear energy spectra of polymers match their relaxation behaviour over a wide range of temperatures. To simulate a viscoelastic relaxation, a sample of polyethylene was torn over a certain length at room temperature, and the tear force was observed to remain constant. The crack was then stopped with a clip and the bent legs of the trouser sample were warmed so that the force registered by the machine fell to a low value, indicating that the polymer legs had drooped fully. The relaxed polymer was cooled to room temperature and the tearing motion restarted. The tearing force was found to be raised as a result of this artificial relaxation, although the intrinsic fracture energy of the material was unchanged. Thus Equation 2 was satisfactorily verified.

To carry out the second experiment, generating a fracture energy spectrum, high-density poly-

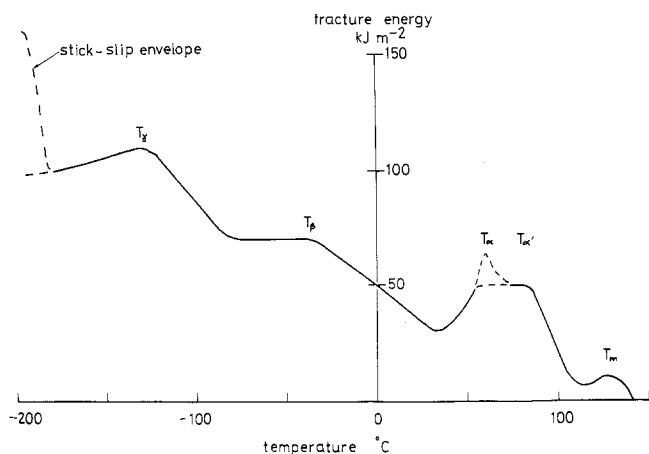


Figure 3 Fracture energy spectrum for high-density polyethylene (Lupolen 5261z) at a crack speed of  $1 \text{ mm min}^{-1}$ .

ethylene was torn at  $1 \text{ mm min}^{-1}$  as the temperature was raised at  $1^\circ \text{C min}^{-1}$  from  $-196$  to  $140^\circ \text{C}$ . The results are plotted in Fig. 3 for comparison with commonly accepted temperatures for viscoelastic transitions in polyethylene [15, 16]. Clearly, the fracture energy reflects the crystalline melting point around  $130^\circ \text{C}$ , the two  $\alpha$  relaxations near  $70^\circ \text{C}$ , the  $\beta$  transition about  $-30^\circ \text{C}$  and the  $\gamma$  relaxation or glass transition at  $-130^\circ \text{C}$ .

A fracture energy spectrum, generated by the same technique for polyvinylchloride, is illustrated in Fig. 4. The glass transition near  $80^\circ \text{C}$  and the  $\beta$  transition around  $-10^\circ \text{C}$  are clearly discernible [3].

These ideas are stimulating in both experimental and theoretical aspects. Theoretically, viscoelastic fracture has been in a complicated state [17, 18] and it has been difficult to understand how viscoelastic losses influence ultimate properties. The simplicity of the theory of tearing embodied in Equations 1 and 2, and the possibility of introducing artificial, model relaxations into the tearing system have shown that the fracture surface energy measured by a tearing test is strongly influenced by mechanical relaxations.

On the experimental side, the connection between polymer failure and viscoelastic transitions has been tenuous, despite the judicious activities of polymer blenders who have striven to improve properties through the introduction of low temperature rubbery transitions [19–21]. Although it has long been suspected that polymer failure is somehow influenced by viscoelastic losses, this influence is not always evident in

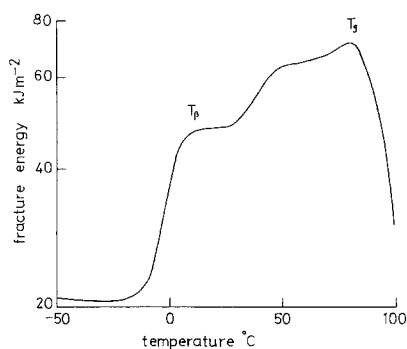


Figure 4 Fracture energy spectrum for polyvinylchloride (Corvic D60/11) at a crack speed of  $2.5 \text{ mm min}^{-1}$ .

tensile strength measurements but appears in tearing and energy loss measurements on rubbers [22–24] and also in the relation between peel strength and viscoelastic properties of rubbery adhesives [25–27]. In particular there has been much interest in the idea that good impact resistance in polymers stems from low temperature mechanical loss peaks [3–6]. Now, Figs. 3 and 4 conclusively demonstrate how fracture surface energy reflects the viscoelastic transitions.

#### Acknowledgement

Thanks are due to D. J. Bye and H. F. Brown for experimental support.

#### References

1. R. S. RIVLIN and A. G. THOMAS, *J. Polymer Sci.* **10** (1953) 291.
2. H. W. GREENSMITH, L. MULLINS and A. G. THOMAS, *Trans. Soc. Rheol.* **4** (1960) 174.
3. R. F. BOYER, *Polymer Eng. Sci.* **8** (1968) 161.
4. P. I. VINCENT, *Polymer* **1** (1960) 425.

5. E. G. BOBALEK and R. M. EVANS, *Trans. Soc. Plastics Eng. J.* **1** (1961) 93.
6. J. HEIJBOER, *J. Polymer Sci.* **C16** (1968) 3755.
7. R. S. RIVLIN, *Paint Technol.* **9** (1944) 1.
8. A. A. GRIFFITH, *Phil. Trans. Roy. Soc. Lond.* **221A** (1920) 163.
9. J. W. OBREIMOFF, *Proc. Roy. Soc. Lond.* **A27** (1930) 290.
10. K. KENDALL, *J. Adhesion* **5** (1973) 105.
11. *Idem, ibid* **5** (1973) 179.
12. *Idem, Int. J. Fracture* **11** (1975) 3.
13. *Idem, Proc. Roy. Soc. Lond.* **A341** 91975) 409.
14. *Idem, Acta Met.* (in press).
15. L. E. NIELSEN, "Mechanical Properties of Polymers" (Chapman and Hall, London, 1962) p. 180.
16. I. M. WARD, "Mechanical Properties of Solid Polymers" (Interscience, London, 1971) p. 181.
17. M. L. WILLIAMS, *Int. J. Fracture Mech.* **1** (1965) 292.
18. W. G. KNAUSS, *ibid* **6** (1970) 183.
19. R. BUCHDAHL and L. E. NIELSEN, *J. Appl. Phys.* **21** (1950) 482.
20. J. A. SCHMITT and H. KESKKULA, *J. Appl. Polymer Sci.* **3** (1960) 132.
21. J. A. MANSON and L. H. SPERLING, "Polymer Blends and Composites" (Plenum, London, 1976) pp. 90–116.
22. T. L. SMITH, *J. Polymer Sci.* **32** (1958) 99.
23. L. MULLINS, *Trans. Inst. Rubber Ind.* **35** (1959) 213.
24. K. A. GROSCH, J. A. C. HARWOOD and A. R. PAYNE, *Nature* **212** (1966) 497.
25. D. H. KAELBLE, *J. Adhesion* **1** (1969) 102.
26. A. N. GENT and R. P. PETRICH, *Proc. Roy. Soc. Lond.* **A310** (1969) 433.
27. E. H. ANDREWS and A. J. KINLOCH, *ibid* **A332** (1973) 385.

Received 31 July  
and accepted 20 September 1978.

K. KENDALL\*

ICI Corporate Laboratory,  
The Heath,  
Runcorn,  
Cheshire, UK

\*Now at: ICI Mond Division, Research and Development, The Heath, Runcorn, Cheshire, UK.

#### Four cobalt-base silicide eutectics

Directionally-solidified Co- and Ni-base eutectic alloys have been studied for high-temperature structural applications such as turbine blades or vanes [1, 2]. Eutectics containing carbide fibres have received considerable attention, but several authors [3, 4] have noted that silicide phases would be expected to have better oxidation resistance. In this note, we report the identification and characterization of four aligned Co-base eutectics reinforced with ternary silicides. This work was an extension of earlier work on Co–Si aligned composites [5].

Initial compositions studied were (at.%), 70Co–20M–10Si, where M = W, Mo, Ti, or Nb. Samples about 2.3 cm diameter and 12 cm long were directionally solidified under argon at 0.64 cm h<sup>-1</sup> under a temperature gradient of 100° C cm<sup>-1</sup>. Transverse sections of the final portions to freeze were studied metallographically, and average compositions of the eutectic portions of the microstructure were determined by electron microprobe. New heats were made of these compositions, and directionally solidified under the same conditions. In each case, dendrite-free

aligned eutectic structures were obtained over most of the sample length. It was concluded that these compositions were at or near eutectic composition. In at.%, these compositions were: 79.2Co–12.6W–8.2Si, 77.8Co–12.3Mo–9.9Si, 76.3Co–17.4Ti–6.3Si, and 82.1Co–10.0Nb–7.9Si.

Transverse microstructures are shown in Fig. 1. The silicide phases were rods in the W (Fig. 1a) and Mo (Fig. 1b) eutectics and lamellae in the Ti (Fig. 1c) and Nb (Fig. 1d) eutectics. A cellular structure disturbed the alignment in the W alloy, and portions of the Ti alloy contained a small volume fraction of isolated carbide particles. Debye–Scherrer X-ray analysis and microprobe measurements indicated that the silicide phase was the hexagonal Laves  $\lambda_1$ -phase (MgZn<sub>2</sub> structure) in the W, Mo, and Ti alloys, but was probably the cubic G-phase (Mg<sub>6</sub>Cu<sub>16</sub>Si<sub>7</sub> structure, denoted T in the Russian literature) in the Nb alloy. The established phase diagrams show that the Co solid solution is in equilibrium with the  $\lambda_1$  phase in the Co–W–Si [6] and Co–Mo–Si [7] systems, and is in equilibrium with both the  $\lambda_1$  phase and the G phase in the Co–Ti–Si [8] and Co–Nb–Si [9] systems.