JOURNAL OF MATERIALS SCIENCE 28 (1993) 4841–4845

Modes of stress–strain curve distribution for modacrylic fibres

JIN-SHY TSAI
Catalyst Research Center, CTCI, PO Box 88, Toufen, Miaoli, Taiwan

Modacrylic fibres produced by acrylonitrile and vinylidene chloride copolymers possess a high degree of flame-resistance and have four modes of the stress–strain curve distribution. The yarn consisting of filament fibres spun from one spinnerete has the mechanical properties of a blend and is used for the production of staple fibre by the draft method. From the results it can be seen that the mode is controlled by the composition of modacrylic fibre and by the spinning conditions.

1. Introduction

Acrylic fibres are recognized by the rules of the US Federal Trade Commission as a manufactured fibre in which the fibre-forming substance is any long-chain synthetic polymer composed of at least 85% by weight of acrylonitrile chain. The modacrylics commercially available contain 25–60% of comonomers such as vinyl chloride or vinylidene chloride, and consequently possess a high degree of flame-resistance. Since the acrylonitrile and vinylidene chloride copolymerization can be carried out at atmospheric pressure, the production of these copolymers is extremely advantageous from the industrial viewpoint due to the low cost of apparatus and high production efficiency. Furthermore, vinylidene chloride copolymer contains a larger limiting oxygen index (LOI) than vinyl chloride copolymer [1].

Many catalysts or initiators can be used for the polymerization or copolymerization of acrylonitrile. The redox catalysts sodium bisulphite, ammonium persulphate and ferrous sulphate are very good for the suspension polymerization of modacrylic fibre [2]. During wet-spinning with N,N-dimethylacetamide (DMAC) solvent the cross-section shape and structure of modacrylic fibre can be controlled by spinning conditions such as the temperature and concentration in the coagulation bath [3]. The modacrylic fibre spun with DMAC solvent exhibits a higher LOI value and higher water adsorption [4].

The mechanical properties of the fibre also are of importance for modacrylic fibre. In this study it can be seen that changes from a normal stress–strain curve (S–S curve) distribution among fibres, meaning that the coefficient of variation (CV%) of strain and stress (or tenacity) has a very low value, to other modes of S–S curve distribution can be controlled by the doping and spinning conditions.

2. Experimental procedure

The acrylonitrile–vinylidene chloride ($AN–VCl_2$) copolymers used in this study were copolymerized by the suspension method with redox catalysts such as sodium hydrogen sulphite, ammonium persulphate and ferrous sulphate, at 25 °C under nitrogen gas. The slurry of polymer was filtered by centrifugation to form polymeric powder; simultaneously the polymeric powder was washed several times with water, then dried in a vacuum even at 100 °C. The spinning dope contained 24% of the polymer in DMAC, and was spun through a coagulation bath (55% DMAC at 40 °C) to form modacrylic fibre which was stretched in boiling water and dried.

The chlorine content in the polymer was measured by the thermal method [5]. The average molecular weight of the polymer was determined by a Waters model 440 gel-permeation chromatograph with monodisperse polystyrenes as standards. The mechanical properties of modacrylic fibre were determined using a Vibrodyn (Lenzing AG) with a testing speed of 10 mm min^{-1} and a testing gauge of 20 mm, and the mechanical properties of yarn were determined by an Instron 4206. A Cambridge S-360, scanning electron microscope (SEM) was used to examine the cross-section and longitudinal section of modacrylic fibre.

3. Results and discussion

It is well known that the mechanical properties, cross-sectional shape and microstructure of a fibre are largely affected by the composition of polymer, coagulation conditions during wet-spinning [6] and molecular weight of polymer [7]. It is very worthy of note that when $AN–VCl_2$ copolymer is dissolved in DMAC solvent and then spun through the coagulation bath containing DMAC solvent to form modacrylic fibre, modacrylic fibres with different compositions but the same spinning conditions (Table I) exhibit very different mechanical properties, especially the variation (or CV%) of the tenacity, modulus and elongation, as shown in Table II.

The modacrylic fibre containing 50% AN and 50% VCl_2 by weight has a normal S–S curve distribution (Fig. 1), like most textile fibres, among the fibres in the

0022–2461 © *1993 Chapman & Hall*

TABLE I The spinning conditions of modacrylic fibre

Sample	Composition of polymer	Solid content (%)	$\bar{M}_n$ (g mol^{-1})	Drawing ratio
P1	50% AN:50% VCl_2	24	1.24×10^5	8
P2	70% AN:30% VCl_2	24	1.17×10^5	5
P3	70% AN:30% VCl_2	24	1.17×10^5	8
P4	80% AN:20% VCl_2	24	1.09×10^5	5

TABLE II The properties of modacrylic fibre

Sample	Tenacity (g d^{-1})[a]	CV% of tenacity	Modulus (g d^{-1})	CV% of modulus	Elongation (%)	CV% of elongation
P1	2.36	10.11	45	5.03	11.38	9.15
P2	1.91	61.59	58	47.83	8.45	32.38
P3	2.06	46.90	61	35.21	6.75	7.20
P4	1.76	10.66	34	34.49	15.67	22.06

[a] d = denier; g d^{-1} = $1.28 \times \rho \times 10^4$ psi = $8.8335 \times \rho \times 10^{-2}$ GPa, where ρ is the density of the fibre, 1.18.

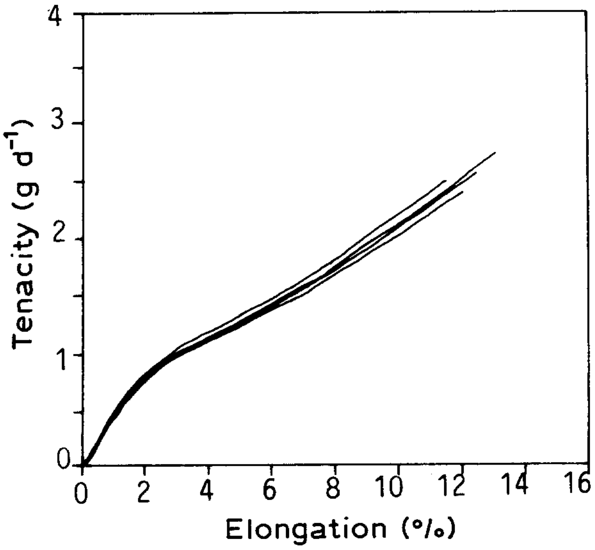

Figure 1 Distribution of S–S curves for modacrylic fibres of sample P1, d = denier (see Table II).

Figure 2 Scanning electron micrograph (× 1000) of the cross-section for modacrylic fibre of sample P1.

yarn or tow spun directly from one spinnerete, i.e. the CV% of the tenacity, modulus and elongation of fibres in the yarn is lower than 10%. The fibre for sample P1 exhibits a cross-section containing many pores at the fringe of the fibre, but exhibits a homogeneous structure near the centre of the fibre, as shown in Fig. 2. Therefore the fibre with this structure tends to a low CV% of the tenacity, modulus and elongation, i.e. the properties among fibres in the yarn are almost the same. The yarn for sample P1 has the S–S curve behaviour shown in Fig. 3.

The modacrylic fibre with 70% AN and 30% VCl_2 by weight exhibits a large CV% of the tenacity and modulus, but exhibits a low CV% of the elongation, as shown in Table II and Fig. 4, due to the change of the coagulation rate which leads a change of the structure of the cross-section as shown in Fig. 5a. This fibre has

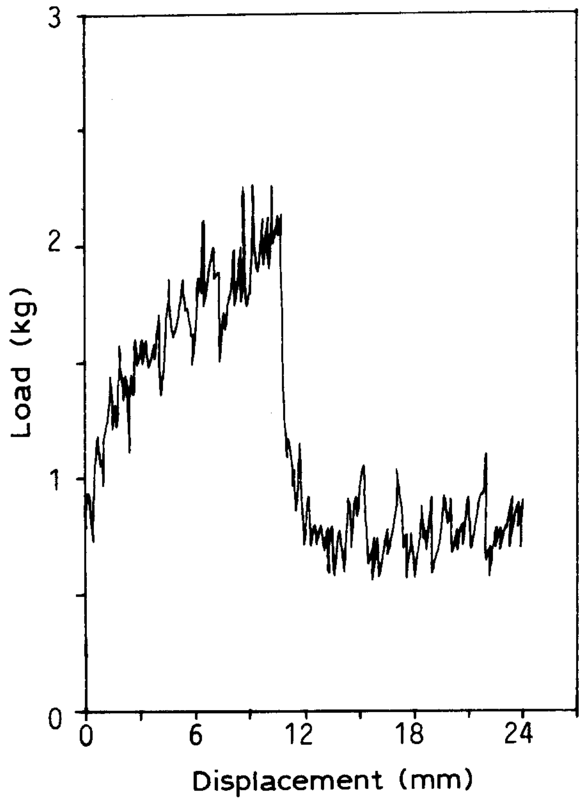

Figure 3 S–S curve of yarn for sample P1.

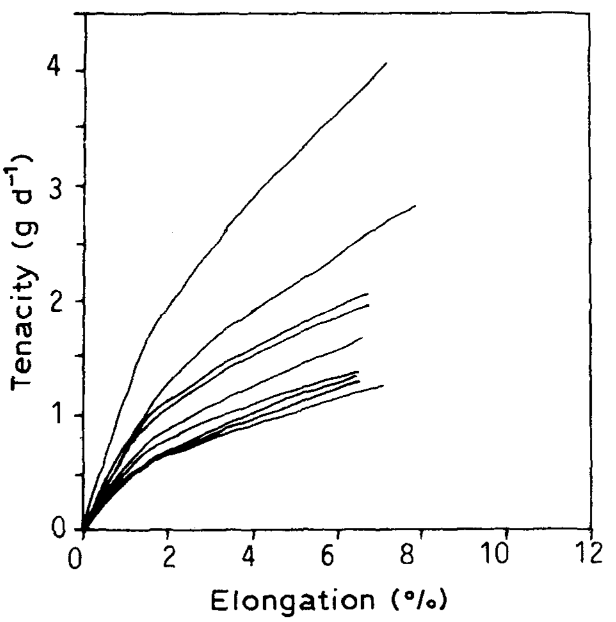

Figure 4 Distribution of S–S curves for modacrylic fibres of sample P3.

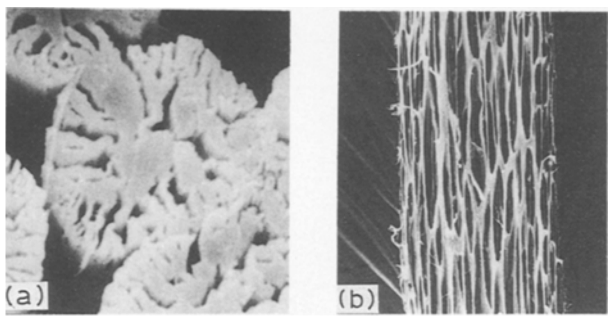

Figure 5 Scanning electron micrograph (× 1000) of (a) cross-section and (b) longitudinal section for modacrylic fibre of sample P3.

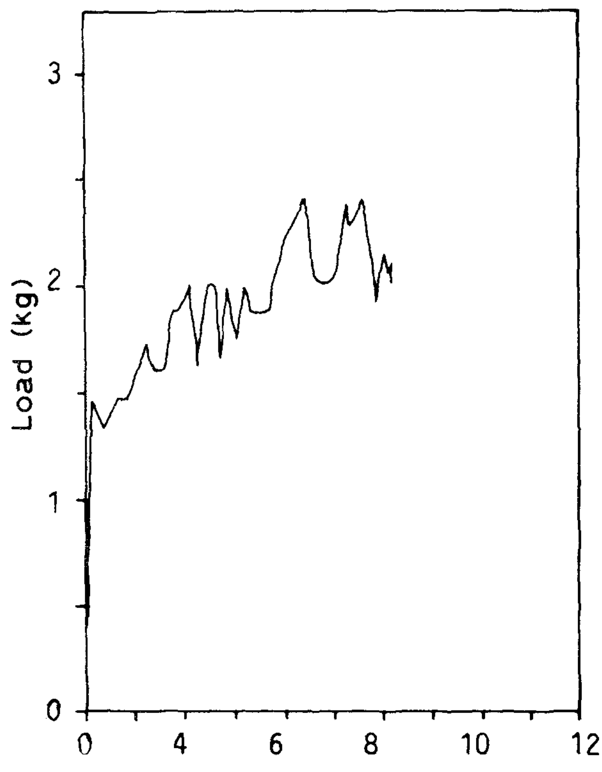

Figure 6 S–S curve of yarn for sample P3.

a net-like structure in the longitudinal section, as shown in Fig. 5b. Because the CV% of the elongation for sample P3 is only 7.2%, the yarn constituted by fibres of sample P3 has a clear breaking point in the S–S curve, as shown in Fig. 6.

If the modacrylic copolymer consists of 70% AN and 30% VCl_2 by weight and is spun to form modacrylic fibre with a drawing ratio of 5, its fibre (sample P2) has a large CV% of the tenacity, modulus and elongation, and has a distribution of S–S curves (Fig. 7) which are quite different to those of sample P1. The structure of the cross-section for sample P2 changes from Fig. 5 to Fig. 8 due to an increase in the drawing ratio. The yarn of these fibres has the mode of a mountain top in the S–S curve, as shown in Fig. 9.

If the modacrylic fibre consists of 80% AN and 20% VCl_2 by weight, the fibres have a distribution of S–S curves with a low CV% of the tenacity and a large CV% of the modulus and elongation, as shown in

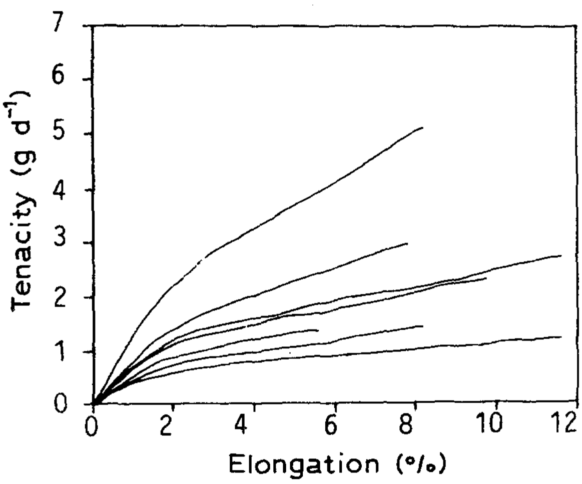

Figure 7 Distribution of S–S curves for modacrylic fibres of sample P2.

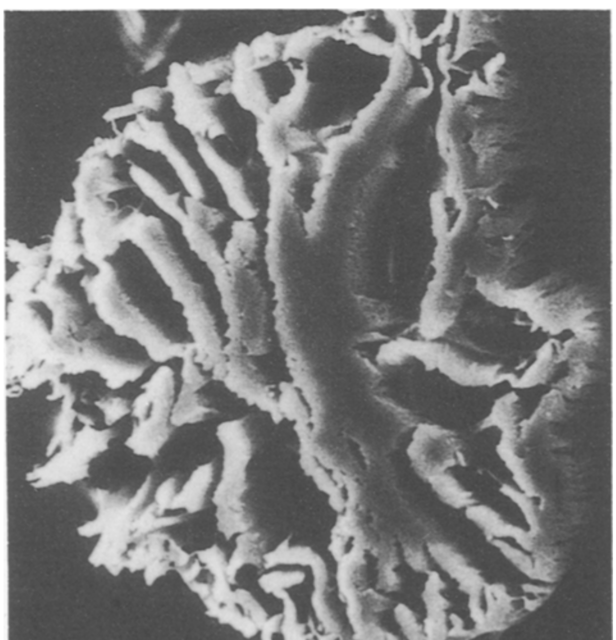

Figure 8 Scanning electron micrograph (× 1000) of the cross-section for modacrylic fibre of sample P2.

Fig. 10. These fibres have a large CV% of the elongation due to the structure of the cross-section as shown in Fig. 11. The yarn of these fibres also exhibits the mode of a mountain top (Fig. 12) which is similar to that of sample P2 due to a large CV% of the elongation.

The modes of S–S curve distribution for modacrylic fibres indicate that the properties of the yarn consisting of these fibres exhibit a blend effect like the blending of many kinds of fibre which have different mechanical properties. Some modes of S–S curve distribution are useful for the production of staple fibres by a draft method.

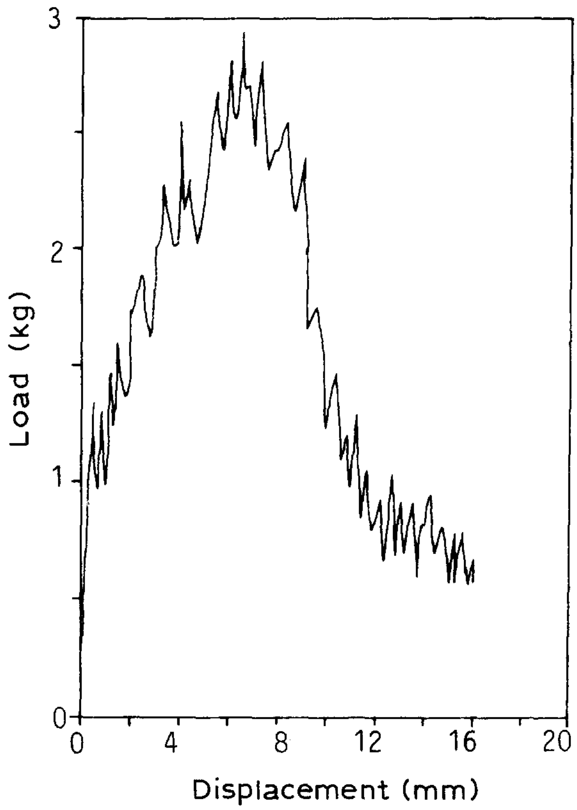

Figure 9 S–S curve of yarn for sample P2.

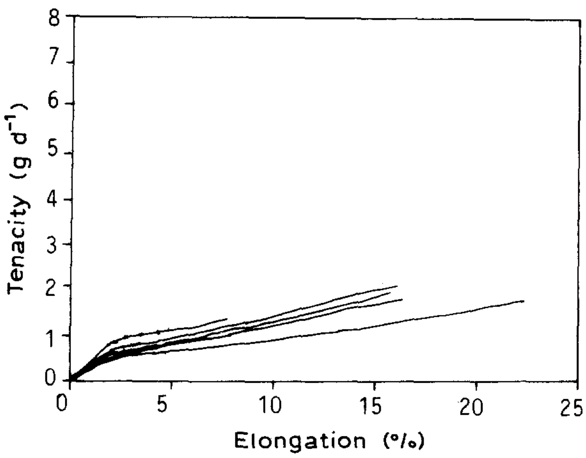

Figure 10 Distribution of S–S curves for modacrylic fibres of sample P4.

Figure 11 Scanning electron micrograph (× 1000) of the cross-section for modacrylic fibre of sample P4.

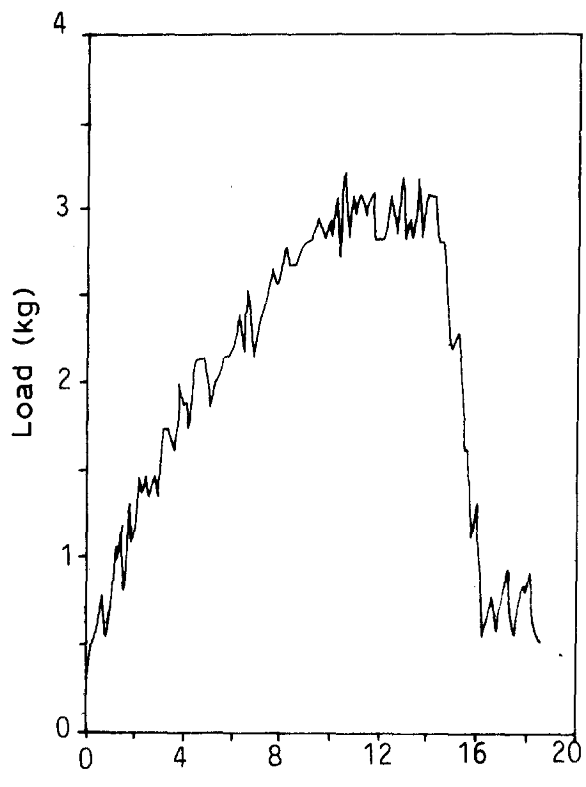

Figure 12 S–S curve of yarn for sample P4.

4. Conclusions

The modes of S–S curve distribution for modacrylic fibre can be controlled by the composition of the copolymer and spinning conditions and the modes involve the following:

(a) The normal mode with a low CV% of the tenacity, modulus and elongation among fibres.

(b) The mode with a large CV% of the tenacity, modulus and elongation among fibres.

(c) The mode with a low CV% of the elongation and a large CV% of the tenacity and modulus among fibres.

(d) The mode with a low CV% of the tenacity and a large CV% of the modulus and elongation among fibres.

References

1. M. LEWIN, S. M. ATLAS and E. M. PEARCE, in "Flame-retardant Polymeric Materials" (Plenum, New York, 1975) p. 16.
2. JIN-SHY TSAI, Chinese patent 52219 (1991).
3. *Idem, J. Mater. Sci. Lett.* **11** (1992) 1017.
4. *Idem, ibid.* **11** (1992) 953.
5. JIN-SHY TSAI, DER-LIN HO and SU-CHI HUNG, *ibid.* **10** (1991) 881.
6. JIN-SHY TSAI and WOEI-CHYI SU, *ibid.* **10** (1991) 1253.
7. JIN-SHY TSAI and CHUNG-HUA LIN, *J. Appl. Polym. Sci.* **42** (1991) 3045.

Received 24 March 1992
and accepted 24 February 1993