Morphology of High-Density/Linear Low-Density Polyethylene Drawn Tapes

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ABSTRACT

The drawn tapes of high-density polyethylene(HDPE) and blends of high-density/linear low-density polyethylene(LLDPE) were made in the composition range of 0–15% LLDPE by melt extrusion and drawing on hot plate. The morphologies of the drawn tapes were investigated through differential scanning calorimetry and scanning electron microscopy after etching with chlorosulphoric acid. The HDPE drawn tape shows a tenacity as high as 650 MPa which rapidly drops to 450 MPa on the incorporation of 10% LLDPE and an improvement of 15% in tenacity thereafter. The elongation-at-break increases linearly throughout the composition range with increase in LLDPE content from 23.5 to 25% . The superiority in tenacity of HDPE drawn tape is due to the greater long folded-chain crystallites (LFCC) and fine diameter, less imperfect, and less branched fibrils. The addition of LLDPE increases the population of short folded-chain crystallites (SFCC). It also transforms a part of LFCC to SFCC. The dimension and imperfection of the fibrils increased as the LLDPE content increased in the drawn tapes. The circular fibrils of HDPE modified to non-circular fibrils on incorporation of LLDPE. It is seen that the fineness of the fibrils improves the tenacity, whereas, the severity in branching reduces it.

Key Words: morphology, HDPE/LLDPE blend, drawn tape, high tenacity, fibril

INTRODUCTION

The morphology essentially controls the properties of drawn polyethylene tapes and fibres. The development of morphology is sensitive to processing techniques. Different morphologies of drawn polyethylene tapes and fibres could be developed through various processing techniques [1–8]. However, certain morphologies are desirable in manufacturing high tenacity tapes/fibres.

The processing techniques recently employed to manufacture high tenacity polyethylene fibre/tapes are gel-like processing of spherulites [1, 2], single crystal drawing [3, 4], virgin polymer drawing [5–7]

and gel spinning [8]. Most of these processes are solvent aided and are environmental polluting and non-economical. The melt extrusion technique is a non-polluting method to manufacture tapes in the most economical way. Furthermore, the melt extrusion technique possesses large number of processing variables hence they assist in developing right kind of morphology. The melt temperature, melt pressure, and on-line stretching of molten extrudate provide easy maneuverability towards the development of morphology. Thus, the melt processing generated a renewed interest in developing high tenacity tapes and fibres.

In an effort to understand the morphology-tenacity correlation, which could help to develop high tenacity and modulus tapes/fibres, the processing variables were stipulated to manufacture high tenacity drawn tape from high density polyethylene.

Small amount of LLDPE, which has almost similar structure and higher degree of branching, was incorporated (in the range of 0–15%) in the HDPE to make HDPE/LLDPE blend drawn tapes with different morphologies. The morphology was then correlated to the tenacity of the drawn tapes.

EXPERIMENTAL

Materials
The HDPE (Hostalene, GF 7745F) used in this study, was a product of Polyolefine Industries Ltd., India. The octene based LLDPE (Dowlex, 2740E), a product of Dow Chemicals, USA, was used as a minor component. Some of the important characteristic properties of both components are presented in Table 1.

Sample Preparation
The tumble mixed HDPE and LLDPE blended in the desired ratio, were extruded through a single screw extruder (Betol 1820, L/D = 17, screw speed 22 rpm) fitted with a bottom fed rectangular 8.0×0.4 mm² slot die. The temperature profile maintained was 160 at feed, 200 at compression, and 210 °C at metering and die zones. The extrudates were stretched on-line to 3 times in the molten condition and then chilled in water at 30 °C. These as-extrudate tapes were drawn

Table 1. Characteristics properties of HDPE and LLDPE.

Properties	HDPE	LLDPE
[η] at 110 °C in Decalin (dL/g)	1.10	1.50
T_m (°C)	131	126
Melt flow index (g/10 min)	0.75	1.00
Density (g/mL)	0.952	0.925
Tensile at yield (MPa)	24.5	19.3
Tensile at break (MPa)	11.4	10.0
CH_3/100 carbon	1.81	3.00
X-ray crystallinity (%)	46	36

on a hot plate of 0.5 m length at 82 °C by 8.4 times at a letting-off speed of 6 m/min.

Subsequent to the drawing process, the drawn tapes were again passed through water maintained at 30 °C and collected in bobbins. The bobbins were kept at 50 °C for 24 h and allowed another maturation time of 24 h at the room temperature before testing were performed.

Tensile Testing
The tenacity and elongation-at-break were evaluated in an Instron Universal tensile testing machine (Model 4310) at a deformation rate of 100% per minute at ambient temperature. The gauge length was 100 mm. A tape grip was used for this study. An average of 20 data points is reported for each group of samples. The tenacity is the ultimate tensile strength of the tape and elongation-at-break is the percentage deformation at the time of failure.

Differential Scanning Calorimetry
The powdered samples weighing about 10 mg were taken in an aluminium crucible and crimped for the differential scanning calorimetry (DSC) experiment on a Perkin-Elmer DSC-7, USA, system.

Under nitrogen blanket, the melting endotherms were recorded at a run rate of 10 °C/min and 1 °C/min. The melting endotherms were normalized against sample weight by employing the software supplied with the system.

The degree of crystallinity is determined as:

$$\text{Crystallinity (\%)} = [\Delta H / \Delta H_c] \times 100 \qquad (1)$$

Where, ΔH is heat of crystallization of the sample and ΔH$_c$ the heat of crystallization of 100% crystalline polyethylene.

Etching of Drawn Tapes

The drawn tapes were suspended freely from a port into chlorosulphoric acid for 24 h at room temperature. The tapes were then washed with distilled water and dried at 60 °C in vacuum.

Scanning Electron Microscopy

The surface of drawn and etched tapes were shaded with silver by vacuum deposition and were photographed by (Stereoscan 360, Cambridge Instrument, UK) scanning electron microscope. Micrographs were taken keeping the electron beam normal to the surface under investigation.

RESULTS AND DISCUSSION

Tenacity and Elongation-at-break of Drawn Tapes

Figure 1 represents the variation of tenacity and elongation-at-break of HDPE/LLDPE blend drawn tapes against weight percentage composition.

As the LLDPE content increases the tenacity decreases non-linearly, whereas, the elongation-at-break increases linearly. A rapid decrease in tenacity from 650 to 450 MPa (i.e., a drop of 30%) is seen by incorporation of 10% LLDPE. The tenacity of a drawn tape containing 15% LLDPE increases significantly after attaining the minimum at 10% LLDPE content. However, the elongation-at-break increases systematically from 23.5 to 25.0%, the pattern
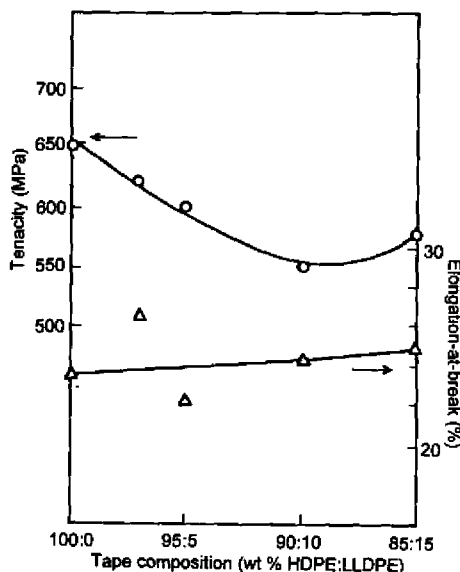

Figure 1. Plot of tenacity and elongation-at-break against blend composition of drawn tapes.

expected from the additivity behaviour [9]. Some of the properties of drawn tapes are listed in Table 2.

It is difficult to appreciate this rapid and disproportionate decrease in tenacity. The addition of 10% LLDPE with slightly inferior tenacity (Table 1 and Figure 2) could not justify this severe drop. The stress
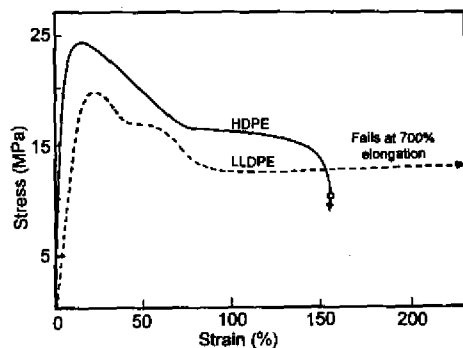
Table 2. Properties of high-density/linear low-density polyethylene drawn tapes.

Properties	HDPE:LLDPE (wt%)				
	100:0	97:7	95:5	90:10	85:15
Denier (g/9000 m)	1160	1286	1242	1440	1332
Initial modulus (MPa)	3976	3092	2872	2194	2632
Density (g/mL)	0.994	0.994	0.994	0.987	0.987

Figure 2. Stress-strain diagram of un-oriented HDPE and LLDPE (adapted from ref.10).
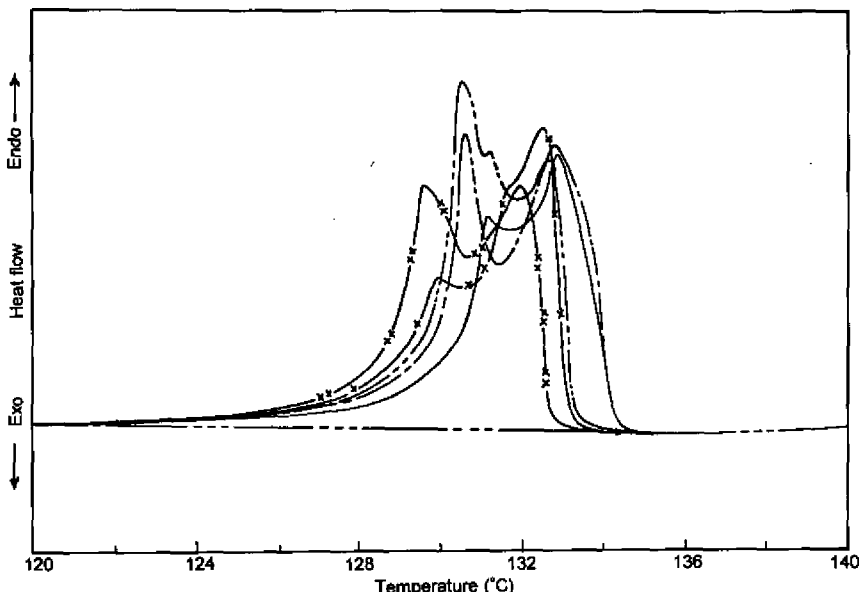
Figure 3. Melting endotherms of drawn tapes at different compositions (wt% LLDPE). (–) 0%, (– –) 3%, (– – –) 5%, (x) 10%, and (xx) 15%

of un-oriented HDPE at the point of break is very close to LLDPE (Figure 2). These close stress [10] values indicate that the large drop in tenacity of drawn tapes on addition of LLDPE may lie in their morphological differences. The subsequent section presents the crystalline morphology of the drawn tapes.

Melting Endotherms of Drawn Tapes
Figure 3 shows the melting endotherms of drawn tapes at a run rate of 1 °C/min. The endotherms are prominently doublet. The first one appears approximately at about 130 °C and the second at about 133 °C. Small shoulders, almost in every composition are present either in the lower or higher temperature side of the lower temperature peak (LTP), i.e., first melting peak and/or to the higher temperature peak (HTP), i.e., second melting peak.

It is quite interesting to notice that the LTP is gradually shifted to the lower temperature side while

the HTP almost maintains its position with the increase in LLDPE content. The melting endotherms at 10 °C/min run rate show similar doublets, however, they are intensely overlapped and because of difficulty in peak separation, they are not presented here. Only the relevant data are shown in Table 3 for reference.

Melting Endotherms of As-extrudate Tapes
The melting endotherms at 10 °C/min run rate, of the as-extrudate tapes in the range of 0–15% LLDPE, are shown in Figure 4. All the endotherms are singlet and peak temperature slightly increase from 130 °C (Table 3) for HDPE to 131.5 °C. The increase in peak temperature indicates an increase in crystal size of HDPE due to the presence of LLDPE. The singlet endotherms are expected due to the co-crystalline [11] characteristics of HDPE and LLDPE.

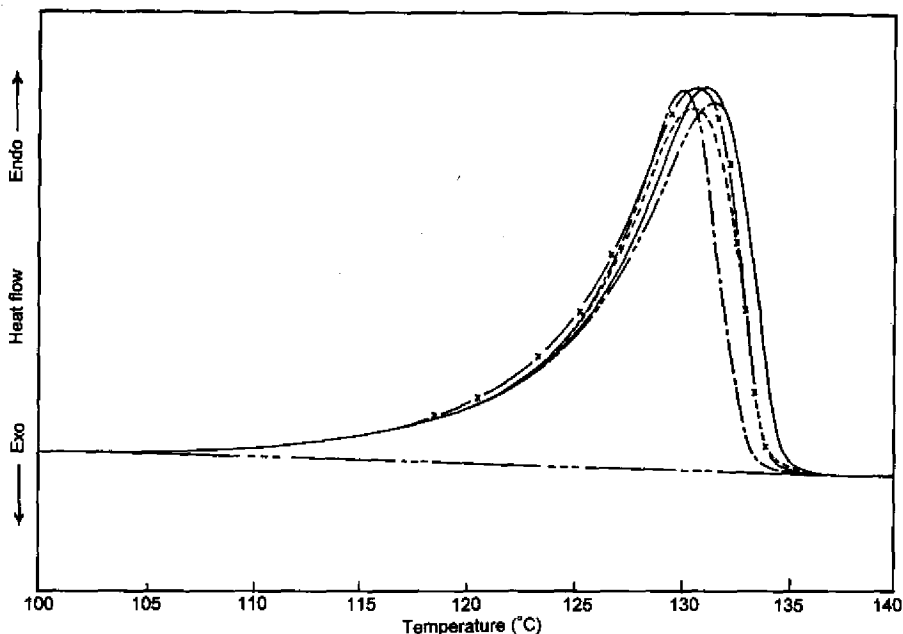The phase separation of HDPE and LLDPE in course of drawing may occur though they show

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Figure 4. Melting endotherm of as-extrudate tapes at different compositions (wt% LLDPE). (–) 0%, (– –) 3%, (x) 5%, (– – –) 10%, and (- - - -) 15%

co-crystalline mass at the as-extrudate stage. Even the drawn HDPE tape shows doublet melting endotherm which itself eliminates the phenomenon of phase separation. Furthermore, the appearance of multiple peaks of gel-spun polyethylene were fibre assigned to the presence of different crystallites [12]. Therefore, the doublet in melting endotherms in the present case may safely be attributed to the presence of at least two types of crystallites in these drawn tapes with varying folded-chain length [13].

The folded-chain length (L) are calculated from the peak temperatures of melting endotherms as per

Table 3. DSC Parameters of as-extrudate and drawn tapes at 10 °C/min run rate.

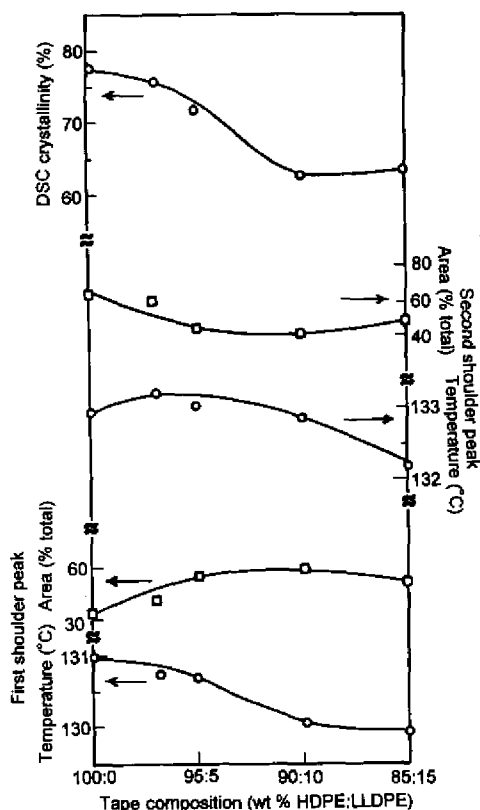| Composition	As-extrudate tape		Drawn tape		
HDPE:LLDPE (wt %)	Crystallinity (%)	Melting peak temp. (°C)	Crystallinity (%)	1st Melting peak temp. (°C)	2nd Melting peak temp. (°C)
100:0	55.0	130.0	62.3	133.0	134.5
97:3	46.0	130.0	62.1	132.5	134.5
95:5	53.0	131.5	62.8	132.0	134.5
90:10	54.5	130.8	58.0	130.5	133.0
85:15	52.0	131.5	57.3	130.5	132.5

Figure 5. Plot of melting characteristic parameters and % crystallinity against blend composition of drawn tapes.

the relationship provided by Wunderlich and Czornj [12] as:

$$L(\text{Å}) = \frac{6.27 \times 414.2}{414.2 - T_m(\text{K})} \qquad (2)$$

where T_m is the melting peak temperature in degree Kelvin.

The folded-chain length is around 220 Å for the type of crystallites melting at 130–131 °C, whereas, the folded-chain length of the other type of crystallites, which melt around 133 °C, is approximately 350 Å. Accordingly the former type of crystallites

are termed as short folded-chain crystallites (SFCC) and the latter one is termed as long folded-chain crystallites (LFCC).

### Characteristic Parameters of Drawn Tapes Endotherms

The variation of peak temperatures and the peak areas under each shoulder [14] expressed as % total area of the melting endotherm. The crystallinity of the drawn tapes are shown in Figure 5. The peak temperature of LTP decreases non-linearly from 131 to 130 °C. The area under LTP shoulder increases non-linearly with the increase in LLDPE content. This increase in area under LTP shoulder is being compensated by the corresponding decrease of peak area of HTP. The peak temperature of HTP slightly increases up to 10% LLDPE content and a rapid drop is seen thereafter.

The percent crystallinity also decreases non-linearly from 78 to 62%, corresponding to a LLDPE content of 10% followed by a retained crystallinity of 62% with 15% LLDPE containing drawn tape.

Both the peak temperature of LTP and % the crystallinity maintained similar decrease to that of tenacity up to 10% LLDPE content. The improvement in tenacity at 15% LLDPE content does not match with the trends of LTP peak temperature and percent crystallinity. The peak area under LTP increases disproportionately from 30 to 60% on addition of 10% LLDPE. This indicates some transformation of LFCC to SFCC as the LLDPE was incorporated. The slight increase in peak temperature of HTP also adds to this belief that some lower melting LFCC might have transformed to SFCC. It has been demonstrated [15] that increase in folded-chain length provides stronger polyethylene. Hence the decrease in folded-chain length of SFCC, as is manifested by the decrease in melting peak temperature of LTP, decreases the tenacity of drawn tapes on addition of LLDPE. The decrease in tenacity seems to be very sensitive to the decrease in folded-chain length of the crystallites. A decrease of 1 °C in peak temperature of LTP causes 30% decrease in tenacity value.

Morphology of Drawn Tapes

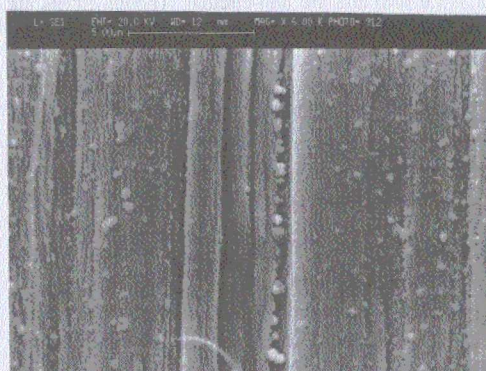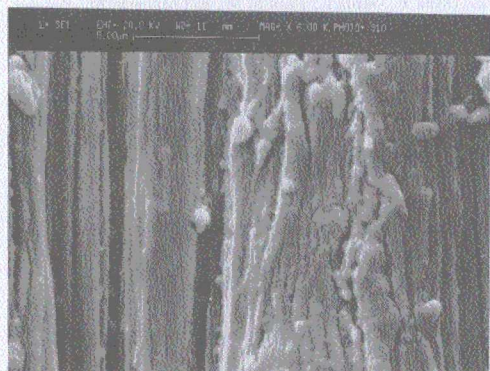Figure 6(a–c) presents the SEM micrographs of drawn
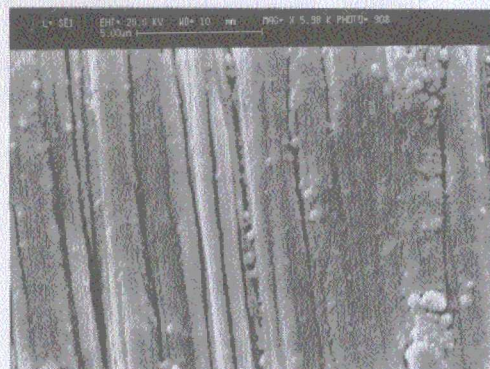
(a)
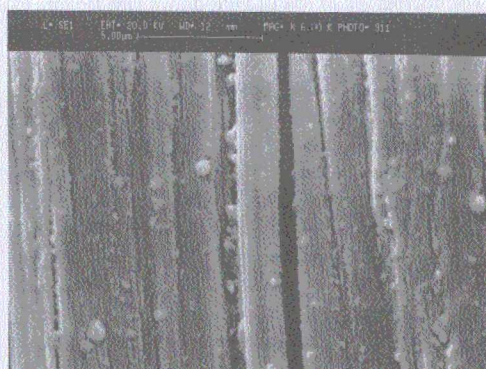
(d)

(b)

(e)

(c)

Figure 6. Scanning electron micrographs of drawn tapes (wt% LLDPE): (a) 0%, (b) 3%, (c) 5%, (d) 10%, (e) 15%.

and chlorosulphoric acid etched tapes in the whole range of compositions. In general, the fibrillar morphology is apparent in all the cases, however these fibrils vary considerably in cross-sectional geometry, fineness and imperfection as the composition changes.

The fibrils of HDPE (Figure 6a) are mostly circular with majority of them maintaining a diameter of 0.7–1.0 μm. These fibrils are thinnest in the whole composition range. Few imperfect fibrils are also visible. These fibrils are almost free of branching.

The micrograph of 3% LLDPE drawn tape (Figure 6b) greatly resembles the micrograph of HDPE except that the fibrils are coarse (diameter varies in the range of 1.2–1.5 μm) and few of them are distinctly branched. Morphology at this composition is almost free of imperfect fibrils.

The morphology of 5% LLDPE drawn tape (Figure 6c) is quite different from the previous two. The fibrils are non-circular, thicker with the average cross-sectional diameter varies from 1.7–2.0 μm. Severe branching is seen at this composition together with imperfection of fibrils.

Figure 6(d-e) presents the micrographs of 10 and 15% LLDPE containing drawn tapes respectively. These fibrils coarse (diameter varies in the range of 2.5–3.0 μm) and are non-circular. Though fibrils are not very prominent and show feeble branching, they are free of imperfect members.

The appearance of fibrils vary greatly at microscopic level. It may be possible to assign doublet of the melting endotherms to the different types of fibrils present, however, that requires extensive investigation. The observed variation in tenacity seems to have good correlation with the fibril fineness, imperfection and branching. The finer and less branched fibrils help HDPE drawn tapes to manifest better tenacity.

The presence of imperfect fibrils indicate the scope of further improvement in tenacity. The tenacity progressively decreases as the fibrils become increasingly thicker and the number of imperfect fibrils increase up to the 5% LLDPE containing blends. This tendency extends to 10% LLDPE containing drawn tape as the diameter increases, which seems to be countered by the reduction in branching of fibrils. The reversal in the drop in tenacity at 15% LLDPE drawn tape arises out of reduction in quantity of branched fibrils.

CONCLUSION

There are at least two types of crystallites, i.e., short folded-chain crystallites and long folded-chain crystallites, seem to be present in HDPE/LLDPE drawn tapes irrespective of their composition.

The HDPE drawn tape shows superior tenacity among the HDPE/LLDPE drawn tapes due to its possessions of: (i) greater number of fine fibrils, (ii) low content of imperfect fibrils, (iii) higher quantity of long folded-chain crystallites, and (iv) high crystallinity. It is shown that, on incorporation of LLDPE the diameter of the fibrils increased, the content of the imperfect fibrils increased up to 10% and reduced thereafter.

The content of the long folded-chain crystallites decreased and conversely, the quantity of short folded-chain crystallites increased. A part of long folded-chain crystallites transformed to short folded-chain crystallites.

All these factors are responsible for the severe and disproportionate drop in tenacity up to 10% LLDPE content of the drawn tapes. Neither the shoulder peak area, nor the peak temperature of both lower temperature and higher temperature shoulder peak suitably explain the increase in tenacity beyond 10% LLDPE content.

However, the SEM morphology consistently explains the tenacity. The increase in fibrillar fineness makes the tape stronger while the encountering of fibrillar branching and imperfection reduces it.

REFERENCES

1. Ohata T., and Okada F., US Patent, 4643865, 1987.
2. Ohata T., Okada F., Hayashi M., and Mihoichi M., *Polymer*, **30**, 2170, 1989.
3. Furuhata K., Yokakawa T., and Miyasaka K., *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 133, 1984.
4. Kanamoto T., Tsuruta A., Tanaka K., Takeda M., and Porter R.S., *Polym. J.*, **15**, 3027, 1983.
5. Smith P., Chanzy H.D., and Rotzinger B.P., *Polym. Commun.*, **26**, 258, 1985.
6. Chanzy H.D., Rotzinger B.P., and Smith P., Patent WO 8703288, 1991
7. Smith P., Chanzy H.D., and Rotzinger B.P., *J. Mater. Sci.*, **22**, 523, 1987.
8. Mark H.F., Bikales M.N., Overberger C.G., and Menges G., *Encyclopedia of Polymer Science and Engineering*, John Wiley, **6**, 493, 1984.

9. Ward I. M., *Mechanical Properties of Solid Polymers*, Wiley, Bristol, 1983.

10. Gupta A.K., Rana S.K., and Deopura B.L., *J. Appl. Polym. Sci.*, **46**, 99, 1992.

11. Gupta A.K., Rana S.K., and Deopura B.L., *J. Appl. Polym. Sci.*, 7, **44**, 719, 1992.

12. Hsiesh Y.L., and Ju J., *J. Appl. Polym. Sci.*, **35**, 347, 1994.

13. Wunderlich B., and Czornj G., *Macromolecules*, **10**, 906, 1977.

14. Paliwal D.K., *Ph.D. Thesis, IIT Delhi*, 74, 1995.

15. Baer E. and Moet A., *High Performance Polymers*, Hanser, 286, 1990.