Studies on Dry-Jet-Wet Spun Polyurethane Fibers. II. Effect of Polyurethane Shore Hardness on Spinnability and Fiber Properties

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ABSTRACT: This article reports a study on the spinnability of three different ester type thermoplastic polyurethanes (TPUs) with shore hardness 75A, 85A, 92A using the dry-jet-wet spinning method. The three grades have been analyzed by FTIR, GPC, and ^{1}H-NMR to establish the difference among them. FTIR indicated that all the three grades were chemically similar and GPC suggests that molecular weight increased with increase in shore hardness. Compositional analysis indicates that the hard segment content increases with increase in shore hardness. Shear viscosity of TPU dope solution increases with increase in shore hardness. Of the three different grades of TPUs studied, only the grades with shore hardness of 85A and 92A are spinnable under the experimental conditions. The fiber properties of three different grades have been compared. Fibers spun with the shore hardness of 85A have good elastomeric properties compared with the other two grades. Lab spun fibers have also been compared with the commercial spandex fibers. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 843–851, 2010

Key words: polyurethane; shore hardness; shear viscosity; spinnability; spandex

INTRODUCTION

Segmented polyurethane elastomers are linear block copolymers of —(HS)n-type (H, hard segment; S, soft segment) whose versatile physical properties are generally attributed to their microphase-separation structure. The microphase-separation structures arise due to the incompatibility of the hard segment and the soft segment. This microdomain two-phase morphology is responsible for the mechanical properties of these elastomers.[1]

Many reports have dealt with the structure and mechanical properties of polyurethanes (PU) in terms of chemical composition,[2] morphology,[3] molecular weight,[4] hard segment content,[5,6] type of components,[7] thermal history,[8] strain rate,[9] the content of triol cross linking agent,[10] and extent of phase segregation.[11–13]

Furguson and Patsovoudis[14–16] in a study, synthesized a series polyurethanes from adiprene L100 (a polyether based macrodiisocyanate) of molecular weight of ∼ 2000, trimethylene diamine, and 4,4′diphenylmethane diisocyanate (MDI). The

molecular weight of the soft segment was kept constant and the size of the hard segment progressively increased, such that the final product in the series was not polyurethane, but a polyurea. These were wet spun into fibers and their tensile[14] and dynamic mechanical properties[15] were measured. It was found that their specific breaking stress, elongation, elastic recovery, and stress relaxation characteristics were all dependent on soft segment (polyether) concentration. A transitional region appeared at ∼ 50% soft segment/50% hard segment concentration. They also observed that the polyurethane fibers spun by a polymer with 70.8% of soft segment content had best elastomeric properties.[14] In another study by the same group,[16] they studied the effect of increasing molecular weight of soft segment while ensuring that the ratios of soft to hard segment content in PU remained constant. They reported similar observation in properties, although there was a slight deterioration in physical properties with higher soft segment molecular weight. They opined that the reason for best elastomeric properties of polyurethane at soft segment content of 70.8% is that at this percentage of soft segment, the soft segment is in continuous phase and hard segment content is in the discontinuous phase and the fiber properties are primarily decided by the soft segment content.

Shore hardness Type A is a measure of viscoelastic properties of rubber type elastomeric

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materials. It is basically a measure of the resistance of the material to micro indentation. Each 0.001 inch of deflection of the indenter is shown as 1° Shore (A); therefore, the harder is the material, the more is the deflection and higher is the value of shore hardness A. Interestingly, there are no reports on how the shore hardness affects the fiber mechanical properties and spinnable characteristics of polyurethanes.

The first part of this article[17] reports optimization of the three important spinning parameters for dry-jet-wet spinning of neat polyurethane with shore hardness 85A, namely, bath ratio, bath temperature, and stretch ratio using Box-Benkhen design. After optimization of these parameters, the effect of percentage dope solid content and dry-jet length were also studied. It was observed that the dry-jet-wet spun polyurethane fiber from TPU with shore hardness 85A has an instantaneous elastic recovery of 64%. In ester type TPUs, it is not known how the shore hardness content affects the fiber properties. Further, how the chemical structures, molecular weight, and the rheological properties vary with shore hardness content is also not known. Hence, the objective of this study would be to further ascertain the most suitable polymer grade with appropriate shore harness for fiber application. Therefore, two grade of TPU with shore hardness one above (92A) and one below (75A) the level of already investigated shore hardness 85A[17] were chosen. To establish the difference among them, they were characterized by gel permeation chromatography (GPC), infrared spectroscopy (FTIR), nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR), and rheological properties (shear viscosity). The spinnability performance of all the three grades was tested under the optimized spinning parameters obtained in the previous study with the grade GP85AE.[17] Finally, the dry-jet-wet spun TPU fibers were characterized for physical properties and morphological features, and the effect of shore hardness of PU on the spinnability and fiber properties were studied.

EXPERIMENTAL

Materials and methods

The thermoplastic polyurethane (TPU) used in this study was Elastane® supplied by Noveon, Belgium. The three grades GP75AE, GP85AE, and GP92AE are ester type with shore hardness 75A, 85A, and 92 A, respectively. Dimethylformamide (DMF) Lab grade from Merck (India) was used as supplied. The nonsolvent used in the experiment was double distilled water prepared in our laboratory, which had a pH of 7.0.

Spinning

The fiber spinning was carried out on a solution-spinning machine supplied by Bradford University Research with single hole spinneret of 0.3 mm diameter. The polymer dope solution of required solid content (w/w) was prepared by dissolving requisite quantity of polymer chips and DMF in the reaction tube having a mercury seal and mechanical stirrer attached. The whole mixture was stirred until a clear solution was obtained; subsequently, it was deaerated in vacuum at 45°C for 30 min to remove air bubbles. Fiber spinning was carried out with optimized spinning parameters reported in the previous paper.[17] As the dope solution viscosity varied drastically with the shore A hardness content of PU, the fiber spinnings were done at comparable Ball Fall viscosity. The ram speed and first take up roller speed were kept at 0.1 mm/min and 4.2 m/min, respectively.

Characterization

The molecular weight was determined using Hitachi LaChrom Elite GPC with Hitachi L2490 RI Detector and Hitachi L-2130 pump. Tetrahydrofuran (THF) as a solvent was used with a flow rate of 0.1 mL/min through Stragel columns. The average molecular weight of the samples was calculated in equivalent polystyrene with the calibration curve established from standard samples of polystyrene.

Fourier infrared spectroscopy (FTIR) experiments were performed with PerkinElmer spectrometer at a resolution of 4 cm^{-1}. Thin polyurethane films very prepared by solution casting 5% PU solution on aluminum foil. The films were dried in vacuum oven at 50°C for 24 h to remove DMF.

All the nuclear magnetic resonance (NMR) experiments were recorded on Brucker DPX 300 MHz NMR spectrometer. The NMR measurements of the polymer were carried out using deuteriated dimethylsulfoxide (DMSO) at 60°C. The ^{1}H-NMR spectra for all the samples were recorded at a frequency of 300.13 MHz. The standard pulse sequence given in Bruker pulse program library was used for the recording. The 32K data points were accumulated with 5 s delay time between 16 successive scans. The ^{13}C-NMR spectra of all the samples were recorded at 75.5 MHz. A total of 6000 scans were accumulated with a relaxation delay of 2 s containing 64 K data points.

The rheological properties of polyurethane in DMF solution were studied by both Brookfield shear viscometer and ball fall methods. Shear viscosity was measured on a Brookfield viscometer at 45°C with spindle no. BS 29 from 5 to 100 rpm. The ball fall viscosity of the TPU/dope solution was measured using a ball fall viscometer tube of 2.5 cm

diameter. The tube was filled with dope solution till the marked point and placed in a water bath maintained at 45°C (same as the spinning dope temperature). A steel ball of 1/8 inch (0.32 cm) in diameter and weighing 0.13 g was dropped in the viscous solution. The time taken by the steel ball to traverse a distance of 20 cm through the polymer solution is taken as the ball fall viscosity measured in seconds. An average of 10 readings was taken.

Linear density of the material was tested according to ASTM standard D2591. The linear density of the PU GP85AE spun filaments were in the range of 185 (±5.5), 145 (±5.8), 120 (±6), 110 (±4.5), and 90 (±3) denier for stretch ratios of 1.2, 1.5, 1.8, 2.0, and 2.5, respectively. The linear density of the PU GP92AE spun filaments were in the range of 183 (±4), 144 (±5), and 118 (±5.6) denier for stretch ratios of 1.2, 1.5, and 1.8, respectively. The unit of linear density used here is denier, which is the weight of 9000 m of fiber length in grams. The commercial Lycra monofilament used for comparative study was supplied by INVISTA and its linear density is 80 (±3.5) denier.

Tensile tests were carried out on Instron 4301 (U.K.) with a crosshead speed of 450 mm/min and gage length of 25 mm. The regular fiber jaws were modified by neoprene rubber liners to avoid the filament slippage. The filaments were held at a pretension of 0.05 mN/tex before tightening the jaws. All the results reported are an average of 10 specimens.

Elastic recovery (ASTM D2731) tests were carried out on an Instron model 4301 universal testing machine using 10 specimens of each material. Five-centimeter long fiber samples were extended to 300% elongation at a rate of 500 mm/min and allowed to relax. This cycle was repeated five times and, on the fifth cycle, the crosshead is stopped at maximum extension and held for 30 s then relaxed. In the sixth cycle, extension noted at load of 0.05 mN/tex. Permanent deformation (set) is calculated using the following relation:

$$S = (E \times 100)/L$$

where S, permanent set %; E, extension on the sixth cycle at 0.05 mN/tex tension, mm; and L, gage length in mm.

Elastic recovery (ER) % is given by relation: (ER = 100 − S).

The density of PU filaments were measured using the conventional density gradient column supplied by Davenport (London). N-heptane and carbon tetrachloride was used for preparation of density gradient column. The column was calibrated using glass beads of accurately known densities. The measurements were made out on single filament of 1 cm length at 25°C. All the reported results are an average of 10 readings.

TABLE I
Molecular Weights of TPU with Different Shore Hardness

Sample type	Shore hardness	M_n	M_w	Polydispersity index	Density (g/cc)
GP75AE	75A	57248	89809	1.57	1.23
GP85AE	85A	74561	108109	1.45	1.23
GP92AE	92A	88101	142371	1.62	1.22

Sonic velocity was measured on a dynamic modulus tester PPM-5R (H. M. Morgan Co., USA) on samples. The sonic modulus (E_s) is calculated from the expression:

$$E_s \text{ (g/denier)} = 11.3 \times C^2$$

where C is the sonic velocity in km/s. This relationship is independent of density of samples.

Fiber samples for SEM cross section studies was first drawn through soft wooden cork and very thin slice were sectioned using sharp blade and then sputtered with silver. Zeiss Evo® 50 (Germany) scanning electron microscope operated at an accelerating voltage of 20 kV and current of 100 µA was used for scanning the fiber cross section and morphology.

Spinnability

Spinnability studies of all the three grades were carried out under the optimized spinning conditions reported earlier.[17] The optimized conditions are:

Bath Ratio (DMF : Water): 60 : 40
Bath Temperature: 15°C
Stretching Bath Temperature: 48°C
Dope Temperature: 45°C
Solvent: DMF
Air gap length: 20 mm ± 2 mm
Jet stretch: 0.85
Jet stretch ratio = $V_1/<V>$
Stretch ratio = V_3/V_1

where $<V>$ = average velocity of the dope in the spinning hole, i.e., $<V> = Q/\pi R^2$, Q = flow rate per hole (cc/min), and R = spinneret hole radius. V_1 = surface velocity of the first godet, i.e., first roller after coagulation bath, cm^{-1}. V_2 = second roller take up speed, cm^{-1}, V_3 = winding drum speed, cm^{-1}.

RESULTS AND DISCUSSION

GPC analysis

Table I shows the results of GPC analysis. The results suggest that molecular weight of TPU increases with shore hardness and there were no significant differences in their polydispersity index and density.
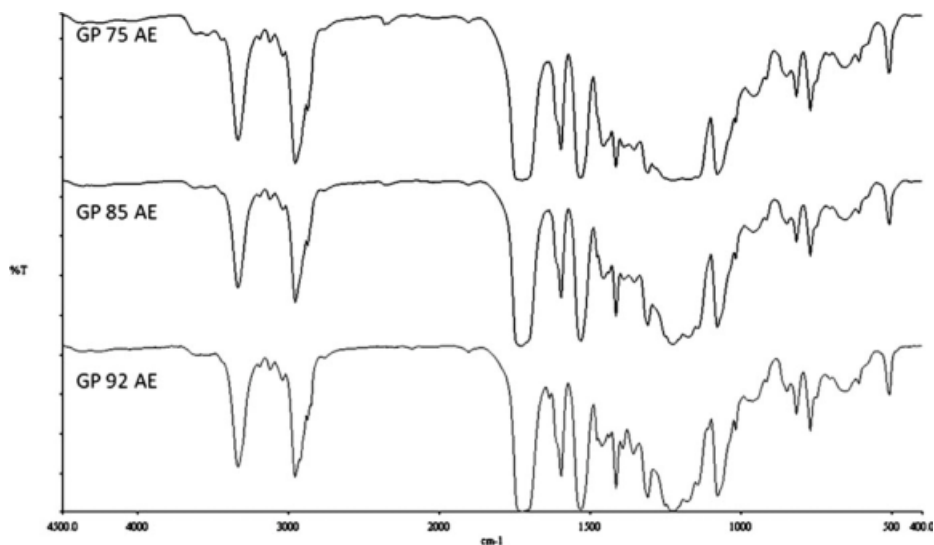
Figure 1   FTIR spectra of TPU with different shore A hardness.

FTIR analysis

FTIR spectra of TPU with varying shore A hardness are presented in the Figure 1. It could be observed that their chemical structure is identical as the characteristic functional group peaks (—NH at ~ 3333 cm^{-1}, —CH at ~ 2860–2940 cm^{-1}, —CO at ~ 1700 cm^{-1}) are same in all the three grades.

NMR analysis

The qualitative characteristics of the different TPUs of varying shore hardness were determined by ^{1}H-NMR spectra (Figs. 2–4). The chemical shift data for the different chemical groups of these TPUs is presented in Table II. Although many methylene groups are chemically identical, their protons are not magnetically equivalent. Complex multiple patterns can also arise due to strong coupling. The X—CH$_2$—CH$_2$—CH$_2$—CH$_2$—X structures occur in polyester polyol and chain extender, i.e., 1,4-BD (1,4-butane diol), so the higher field multiplet is attributable to the internal methylene group, and its chemical shift is less influenced by the attached group (X) than in the adjacent methylene.[18] Thus, the chemical shifts of δ 1.51–1.59 ppm and δ 1.67–1.68 ppm

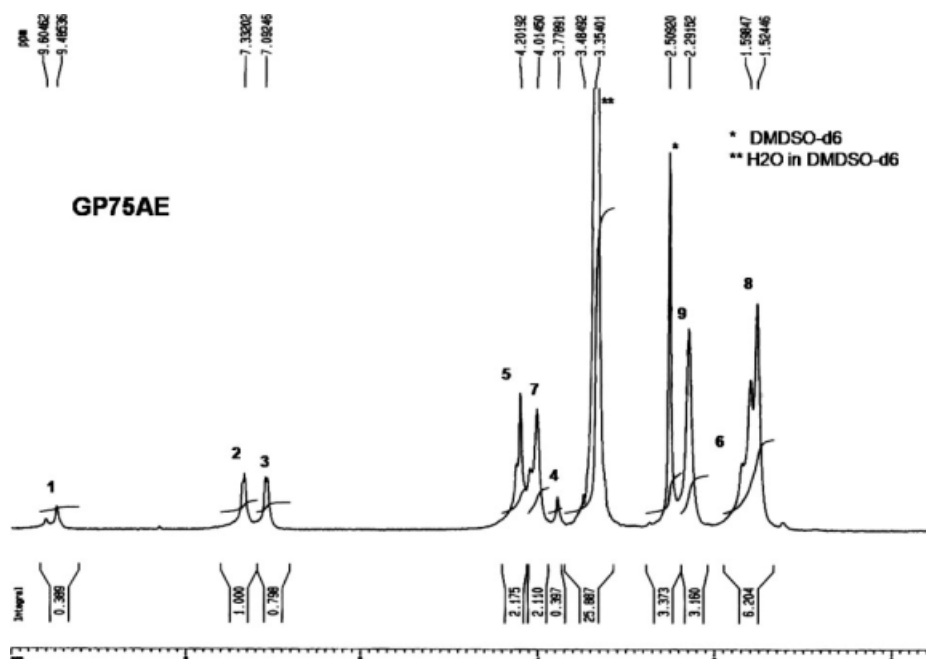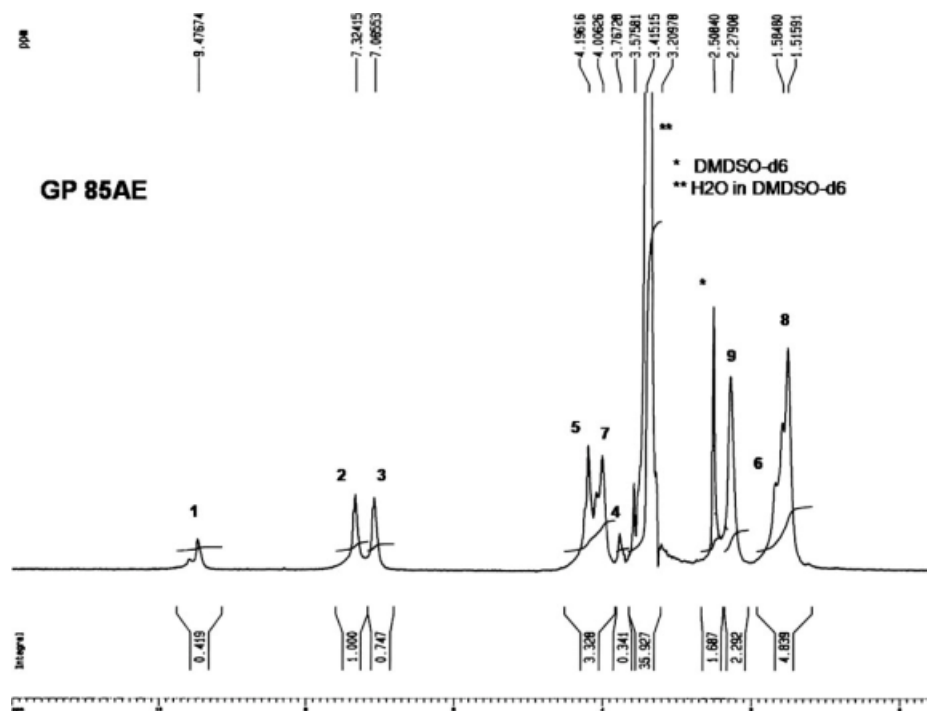**Figure 2**   ^{1}H-NMR spectrum of TPU GP75AE.

Figure 3 ^{1}H-NMR spectrum of TPU GP85AE.

correspond for aliphatic acid of ester polyol and chain extender, respectively. However, the adjacent methylene group displayed chemical shifts of δ 4.01–4.08 ppm and δ 4.19–4.2 ppm for aliphatic acid and chain extender, respectively, when it was adjacent to a urethane group. The methylene group of polyester polyol adjacent to carbonyl carbon of ester displayed chemical shift of δ 2.1–2.24. The diisocyanate group of PU was identified by the NMR spectra and there was a clear CH$_2$ resonance at δ 3.76–3.78 ppm and
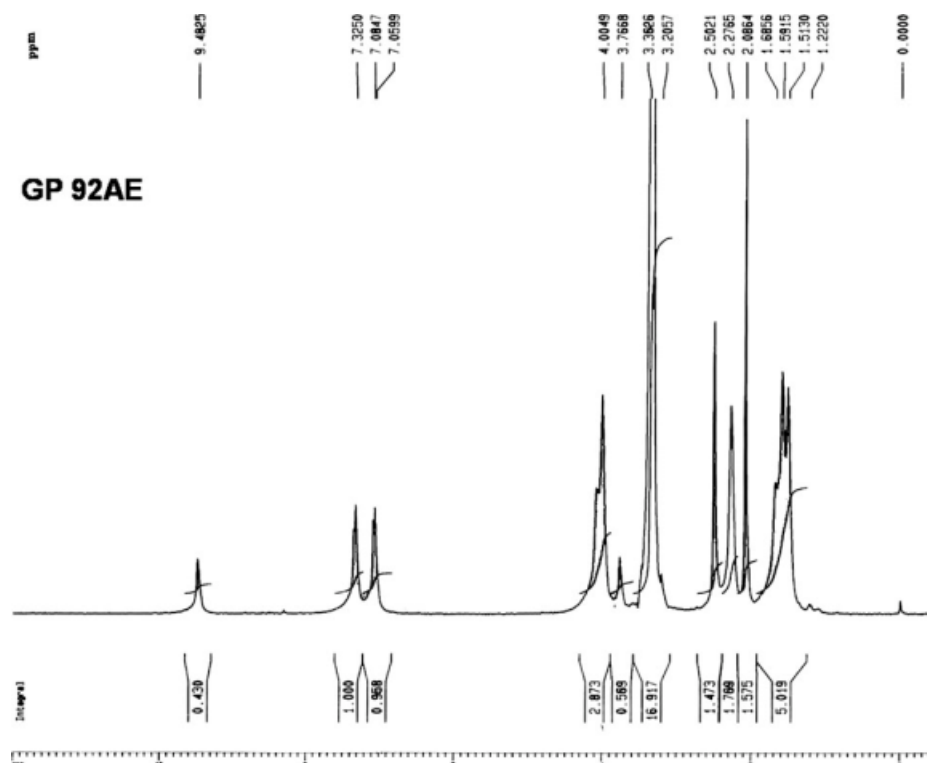

Figure 4 ^{1}H-NMR spectrum of TPU GP92AE.

TABLE II
Structure and Groups of Chemical Shift Data for TPU Samples

Chemical shift (ppm)	Code	Possible groups	Structure
9.476–9.604	1	Urethane proton between MDI and chain extender. Urethane proton between long chain polyol and MDI	
7.32–7.33	(a) 2	Aromatic protons of MDI	
7.05–7.09	(b) 3	Methylene proton of MDI	
3.76–3.78	(c) 4		
4.19–4.2	(a) 5	Methylene of chain extender adjacent to an urethane group	
1.67–1.68	(b) 6	Internal methylene of chain extender adjacent to an urethane group	
4.01–4.08	(a) 7	Methylene of polyester polyol adjacent to an urethane group	
1.51–1.59	(b) 8	Internal methylene of polyester polyol adjacent to an urethane group/carbonyl carbon of ester	
2.1–2.27	9	Methylene of polyester polyol adjacent to carbonyl carbon of ester group	

the aromatic protons were active at δ 7.32–7.33 ppm and δ 7.05–7.06 ppm for 4,4′diphenylmethane diisocyanite (MDI). Similar assignment are also reported in the literature.[18,19] Various carbon resonances were further confirmed by $^{13}C\{^{1}H\}$-NMR spectra.

Compositional analysis

The composition of MDI and polyol content was determined from completely assigned ^{1}H-NMR spectra as shown in Figures 2–4. The intensity of protons in MDI and dihydric alcohols, i.e., chain extender and polyester polyol is used for determination of MDI composition. The MDI composition was calculated using the following relation.

$$\% \text{ MDI content} = \{I_{(MDI\ proton)}/(I_{(MDI\ proton)} + I_{(Dihydric\ alcohol\ proton)})\} \times 100$$

$$\% \text{ Dihydric alcohol content} = 100 - \% \text{ MDI content}$$

Table III indicates that shore hardness of PU is related to percentage MDI content, and hence, shore

hardness increases with MDI content. The hard segments are formed from the chain extension of a diisocyanate with a low molecular weight diol. As MDI is the main constituent of the hard segment responsible for the polar nature of the urethane groups, the increase of MDI content increases the intermolecular attraction in the hard segment due to the inter hydrogen bonding between $-NH^{\delta+}$ and $-C=O^{\delta-}$ groups of hard segment. The hydrogen-bonding index, which is the indication of the degree of hydrogen bonding of the carbonyl group, increases with the increasing hard segment content, regardless of any type of diisocyanate. The hard segment rich

TABLE III
Compositional Analysis Results for TPU with Different Shore Hardness

Polymer type	MDI content %	Dihydric alcohol content %
GP75AE	29.56	70.44
GP85AE	34.42	65.58
GP92AE	40.53	59.47

TABLE IV
Shear Viscosity and Ball Fall Viscosity for TPU of Different Shore Hardness at 45°C

Dope solid content %	Shear viscosity			Ball fall viscosity		
	GP75 AE	GP85 AE	GP92 AE	GP75 AE	GP85 AE	GP92 AE
18	–	–	5600	–	–	37
21	–	–	17,900	–	–	104
24	–	–	a	–	–	313
27	–	3850	–	–	49.7	–
29	–	11,800	–	–	73.8	–
31	3150	17,550	–	25	100.2	–
33	4900	33,550	–	36	202.3	–
36	8800	–	–	54	–	–

[a] Beyond the instrument range.

domain is generally characterized as semi-crystalline and provides stiffness and reinforcement[20] to the polymer, thereby increasing the shore hardness of the TPU. The Brookfield viscosity and Ball fall viscosity data presented in Table IV also testify the explanation given earlier. The increase in viscosity of TPU solution with increasing shore hardness of TPU at same polymer concentration may also be attributed to presence of high hard segment content that enhances the intermolecular interaction, which in turn results in higher degree of hydrogen-bonding index. It is interesting to note that TPUs GP92AE and GP75AE have viscosities that are comparable with regular grade (GP85AE at 27% dope solid content) at dope solid content of 18% and 36%, respectively.

Spinnability of PUs

Spinnability of all the three grades of TPU was compared under the optimized spinning conditions (Table V). In case of GP75AE grade, it does not develop spinnable viscosity at regular 27% dope solid content, and hence, the dope solid content had to be enhanced to 36% to get a spinnable viscosity comparable with the regular grade TPU GP85AE. On the other hand, GP92AE developed a very high viscosity at regular dope solid content, and hence, the dope solid content had to be dropped to 18% to obtain comparable viscosity with the regular grade.

GP75AE TPU was not spinnable into fiber form despite a high dope solid content in the existing set up because the gel fibers were very weak and frequent breaks were encountered in the stretching bath. Further, the gel fibers appeared reddish brown in color, which is typical of the degraded polymer. Therefore, it was concluded that GP75AE was not suitable for fiber spinning. The GP92AE grade PU had very good spinnability at dope solid content of 18% with stretch ratio range of 1.2–1.8 and higher stretch ratio beyond 1.8 were not practical as the fiber breaks were encountered.

As the shore hardness increases, the hard segment composition increases which shifts the morphology from one of discrete hard domains to that of co-continuous hard and soft microphases. From a molecular and segmental orientation point of view and fiber processing and molecular orientation considerations, this co-continuous morphology may hinder fiber processing/stretchability at high shore hardness. On the contrary, at low shore hardness of PU, the hard segment content is largely reduced, and hence, these small discrete hard domains would not give the dope enough strength to spin a fiber.

Properties of PU fibers

Tenacity, elongation, elastic recovery, and sonic modulus properties of the filaments are given in Table VI. The table suggests that the fibers from GP92AE have higher modulus but poor elongation as compared with those from GP85AE PU. This may be due to higher hard segment content, which increases the intermolecular attraction between hard segment due to the hydrogen bonding between —NH and —C=O groups, and hence, enhances the stress and decrease the strain property.[20] The elastic recovery of fibers decreases with increase in shore hardness of PU. Enhancement of the hard segment

TABLE V
Spinnability of Different Grades of TPU at Optimized Spinning Parameters

PU grades	Spinnability					
	Dope solid %					
	18	25	27	31	33	36
GP75AE	–	–	LV	LV	LV	S*
GP85AE	–	S*	S	S	S	S
GP92AE	S	HV	–	–	–	–

LV, low viscosity; HV, high viscosity; S*, spinnable weak fibers; S, spinnable good fibers.

TABLE VI
Comparative Tensile Properties of Filaments Spun from TPU GP92AE at Optimized Spinning Conditions

PU grade	Stretch ratio	Tenacity (g/d)	Elongation (%)	Elastic recovery (%)	Sonic modulus (g/d)
GP92AE	1.2	0.62 (3.0)	587 (2.6)	35 (1.63)	2.66 (0.18)
	1.5	0.55 (2.5)	436 (3.2)	36 (1.35)	2.36 (0.09)
	1.8	0.52 (4.8)	343 (3.8)	33 (0.5)	2.33 (0.05)
GP85AE	1.8	0.58 (4.2)	822 (4.0)	59 (1.5)	0.89 (0.03)

The values in the parenthesis indicate CV%.
Grade GP75AE was not spinnable.

content in PU has been observed to result in decrease of elastic recovery by other researcher's also.[21] As shown in the SEM images of the cross section (Fig. 5), the fibers from GP92AE have irregular cross section as compared with GP85AE fibers. The presence of voids also increases with increase in the stretch ratio (Fig. 5). The decrease in tenacity, elongation, and sonic modulus with increasing stretch may be attributed to these voids which cause stress concentration regions. This may again be attributed to the shift in the morphology from one of discrete hard domain to one of co-continuous hard and soft microphases at high shore hardness/hard segment

content. From molecular orientation and segmental point of view, this co-continuous morphology may hinder stretchability of fiber after coagulation, and hence, result in void formation. Finally, it may be concluded that of all the three grades of PU only GP85AE with shore hardness of 85A had good fiber spinnability and fibers, thus produced possess good elastomeric fiber properties. This may be because at around 65% soft segment concentration, the hard domains are known to be small and the soft segment content is in continuous phase. Therefore, they present only a minor hindrance to the flexible chains capable of flowing quickly to assume equilibrium
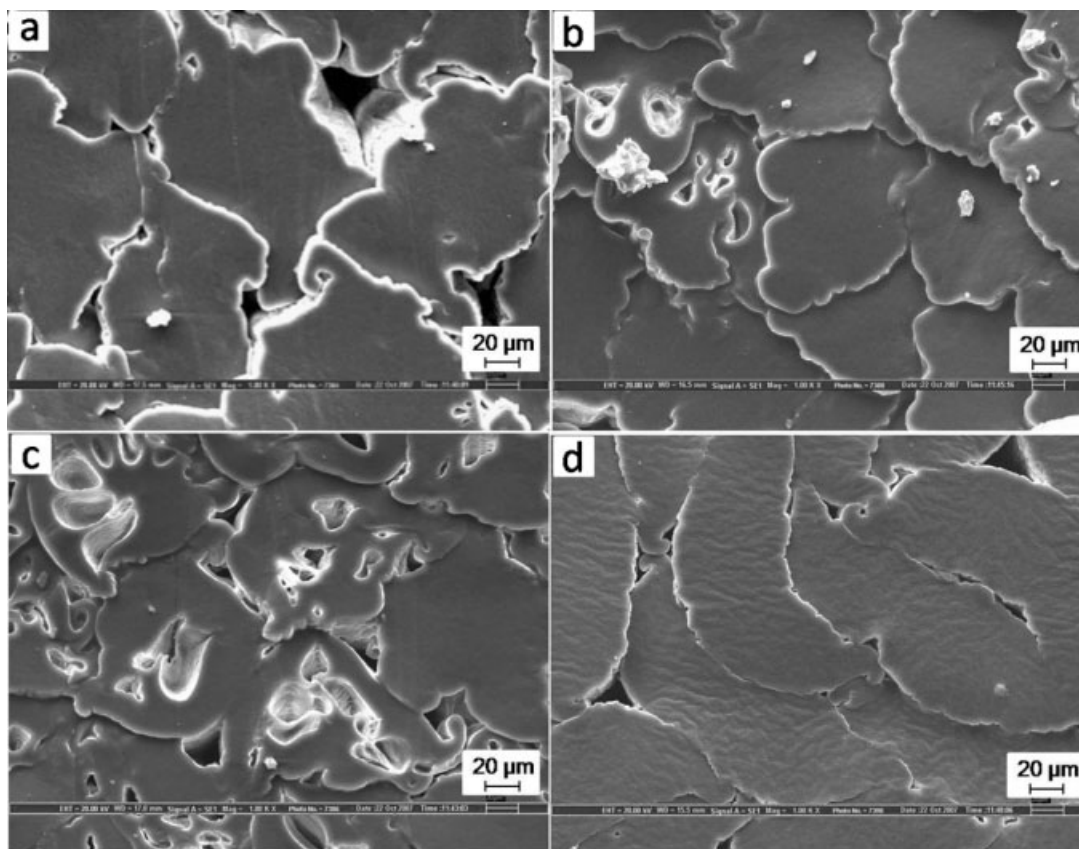

Figure 5 Influence of stretch ratio at optimized spinning parameters: GP 92AE TPU filaments of stretch ratio (a) 1.2, (b) 1.5, (c) 1.8, and (d) GP85AE filament of stretch ratio = 1.8.

TABLE VII
Comparative Mechanical Properties of Commercial Lycra and Spun PU Fibers

Fiber type	Denier	Tenacity (g/d)	Elongation (%)	Elastic recovery (%)
Lycra (commerical)	80 (±3.5)	0.76 (2.4)	689 (5.3)	85 (1.2)
GP85AE (stretch ratio = 2.5)	90 (±3.0)	0.63 (3.7)	611 (6.5)	64 (1.5)

The values in the parenthesis indicate coefficient of variation (CV).

positions as a result of which there would be high and rapid elastic recovery. Thus, we can say the elastomeric fiber properties are primarily decided by the soft segment content when the soft segment concentration is higher $\sim$ 60–65%.

It has been accepted[14,16,22] that the viscoelastic properties of the segmented polyurethane are derived from the interactions of hard and soft segment phases within the polymer. At high soft segment concentration the hard domains are dispersed within the soft segment matrix and act as pseudo cross links preventing viscous flow of the polymer when deformed by external load. Once this is removed, recovery takes place by entropic forces.

Commercial spandex versus laboratory spun fibers

Mechanical properties of commercial Lycra and spun polyurethane fiber (GP85AE) are presented in the Table VII. It is obvious from the table that commercial Lycra fiber has better properties in comparison with the spun fiber. The reason for the differences in the properties of commercial Lycra and lab spun filaments may be attributed to the basic difference in type of polymer used. The lab spun filaments are spun out of thermoplastic extrusion grade PU (Estane GP85AE) which is a linear PU with no chemical cross links, whereas commercial spandex are reported to have cross-linked structure. These chemical cross links in Lycra largely enhance the elastic recovery and improves the tackiness behavior. There could also be differences with respect to the polymer composition, molecular weight, soft to hard segment ratio as well as the spinning and post spinning treatments.

CONCLUSIONS

The molecular weight, hard segment content, and rheological properties of TPU increases with increas-

ing shore hardness as characterized by GPC, ^{1}H-NMR, and shear viscometer.

The spinnability of TPUs with varying shore hardness has been established and their properties correlated to the morphological features.

TPU with shore A hardness of 75A does not possess spinnable properties. Although TPU GP 92AE with shore hardness of 92A has good spinnability, the spun fibers have poor elastomeric properties due to higher void content. TPU with shore hardness 85A has good spinnable and elastomeric properties. This is because at high soft segment concentration the hard domain are dispersed within the soft segment matrix and act as pseudo cross links preventing viscous flow of the polymer when deformed by external load. Once this is removed, recovery takes place by entropic forces. The spun fibers have lower elastic recovery properties as compared with commercial Lycra fibers, the reason may be that the commercial fibers are mostly cross-linked, whereas the lab spun fibers are based on linear thermoplastic PU.

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