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Effect of block molecular weight on the mechanical and dynamic mechanical properties of segmented polyamide

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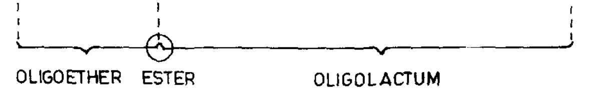
Segmented polyamides also known as polyether-ester-amides, are composed of polyether and polyamide structural units. Dynamic mechanical measurements of these polymers have been carried out over a wide range of temperatures. The polymers with hard block molecular weight of 7400 and 4100 exhibit three peaks, designated as α, β and γ in the tan δ-temperature curve. At a constant soft segment molecular weight of 1000, the α transition shifts to lower temperature and merges with β transition, with decreasing hard block molecular weight. The damping also increases. However, at a constant hard block molecular weight of 1100, though the α and β transitions merge together, the damping decreases on increasing the soft segment molecular weight. The mechanical properties and percent crystallinity decrease with decrease in hard block molecular weight or increase in soft segment molecular weight. The polymers with hard block molecular weight of 7400 and 4100 exhibit a higher set values and yielding characteristics. The results on dynamic mechanical studies are explained with the help of the segmented structure of the block copolymers. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: segmented polyamide; hard block molecular weight)

INTRODUCTION

Block copolymers are multiphase polymers composed of two or more covalently bonded chain segments or blocks that are thermodynamically incompatible. The structural requirement for a block copolymer can be satisfied by several types of molecular architecture. For example, one type is the segmented polyamides composed of polyether and polyamide structural units. The segmented nature of this class of polymers results in copolymers of $(AB)_n$ molecular structure where 'A' represents the soft segment and 'B' corresponds to the hard segment. They are technically very interesting thermoplastic materials of construction, having a broad spectrum of properties. These block copolyamides consist of alternate hard polyamide blocks and soft poly(tetra-methylene-ether) glycol segments. Since the structural units are linked via an ester group, such systems are also referred to as polyether-ester-amides[1] having the chain structure as shown below.



$$H\!-\!\left\{O\!-\![(CH_2)_k\!-\!O]_x\!-\![\overset{\overset{O}{\|}}{C}\!-\!(CH_2)_l\!-\!\overset{\overset{H}{|}}{N}]_{y_1}\!-\!\overset{\overset{O}{\|}}{C}\!-\!(CH_2)_m\!-\!\overset{\overset{O}{\|}}{C}\!-\![\overset{\overset{H}{|}}{N}\!-\!(CH_2)_l\!-\!\overset{\overset{O}{\|}}{C}]_{y_2}\right\}_{n/2}\!-\!H$$

STRUCTURE OF POLYETHER-ESTER-AMIDES

The technological properties of these segmented polyamides can be varied in a controlled manner, not only by using chemically different oligoethers and/or oligolactums but also by varying the average block length. The soft polyether segments account for the flexible character of the polymer, while the degree of molecular association within the polyamide hard segments results in pseudocrosslinks.

Due to the polar nature of the amide groups in the hard segment, and their ability to form hydrogen bonds, these hard segments may form intra- as well as inter-molecular hydrogen bonding coupled with strong dipole–dipole interaction, which possibly leads to domain segregation. The extent of this microphase segregation appears to be dependent on the amount of association between the hard segment units and the relative degree of compatibility between the soft segment chains and the hard segment blocks.

The dynamic mechanical properties of these polymers are expected to respond to the modifications in either the hard block or soft segments or both. Prior to this study, investigations on the dynamic mechanical behaviour of various block copolymers were carried out[2–5]. Typical responses observed for block copolymers are: the lower temperature glass transition region appears to be influenced primarily by the degree of flexibility of the amorphous soft segments and their interactions with the hard segments. The higher temperature relaxation region is controlled mainly by the extent of association of the rigid hard segments. In addition, the relative molecular weights of the hard and soft segments affect the level of the plateau modulus at temperatures between the major relaxation regions. From a review of literature, it is revealed that there is no detailed study in understanding the structure–property relationship in segmented polyamide unlike other polymeric materials. Mayer and co-workers[6] reported the preliminary

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Table 1 M_n, x, $y_1 + y_2$ of PTHF and PA segments, hardness and melting point of different segmented polyamides[a]

Samples	D.s.c. melting point (°C)	Shore hardness *D*	PTHF segment		PA segment	
			M_n	x	M_n	$y_1 + y_2$
M^{a}_{H7400}	174	68	1000	14	7400	37
M_{H4100}	171	62	1000	14	4100	21
M_{H2300}	166	55	1000	14	2300	11
M_{H1500}	156	47	1000	14	1500	7
M_{H1100}	151	40	1000	14	1100	5
M_{S650}	152	53	650	9	1200	6
M_{S1400}	150	35	1400	19	1100	5
M_{S2000}	153	30	2000	28	1100	5

[a] In the structure shown in the Introduction, $k = 4$ (polytetrahydrofuran); $l = 11$ (laurolactum); $m = 12$ (dodecanoic acid; $n = 70–100$; x indicates the length of the soft block, while $y_1 + y_2$ indicates the length of the hard block
[b] Here M_H denotes variation of hard block molecular weight at a constant soft segment molecular weight of 1000. But M_S denotes variation of soft segment molecular weight at a constant hard block molecular weight of 1100. The numbers such as 7400 or 650 occurring in the prefix of M_H or M_S denote the corresponding hard lock or soft segment molecular weight

thermo-mechanical properties of a few segmented polyamides. The technological properties of a few commercial Vestamid polymers were also discussed[7].

The present article reports the results of our studies on mechanical and dynamic mechanical properties of the segmented polyamide block copolymers, with respect to variation of molecular weight in the hard and soft segments.

EXPERIMENTAL

Materials used

Vestamid polymers with specific gravity in the range 1.01–1.02 and different Shore-D hardness were obtained from Hüls AG, Germany. Molecular weight (M_n) variations were made in the hard and soft blocks. *Table 1* lists the M_n of PTHF and PA segments, melting point and hardness of the Vestamid polymers used in this investigation.

Sample preparation

All the samples were initially softened under compression between teflon sheets at 25°C above their respective melting point at 4 MPa pressure. The sheets obtained, thereby, were finally compression moulded at the same temperature and pressure for about 5 min. At the end of the specified moulding time, the sample still under compression was cooled by circulating water at room temperature through the platens until the temperature dropped to 50°C.

Dynamic property measurements

Dynamic mechanical properties under bending mode were evaluated using DMTA (Model No. MK-II, Polymer Laboratories, UK). The frequencies selected were 0.01, 0.1, 1 and 10 Hz. A double strain amplitude of 64 μm was used. The experiments were carried out from −120 to +150°C at the heating rate of 2°C min^{-1}. The data were recorded and analysed by a COMPAQ computer.

Tensile testing

Tensile strength, modulus and elongation at break were measured as per ASTM D412-80 in a computerized Zwick UTM (1445) at a crosshead speed of 500 mm min^{-1}. The dumb-bell-shaped specimens were obtained from the moulded sheets.

Hysteresis study

The hysteresis was obtained on tensile dumb-bell specimen at 100% elongation at a rate of 500 mm min^{-1} at 25°C. The hysteresis ratio (H_R) was calculated using the following formulae.

$$H_R - \frac{W_E - W_R}{W_E} = \frac{\Delta W}{W_E} \tag{1}$$

where W_E = work done during extension; W_R = work done during retraction. The tensile set was also determined from this experiment.

X-ray study

X-ray studies of the samples were performed with a Philips X-ray Diffractometer (type PW1340) using a

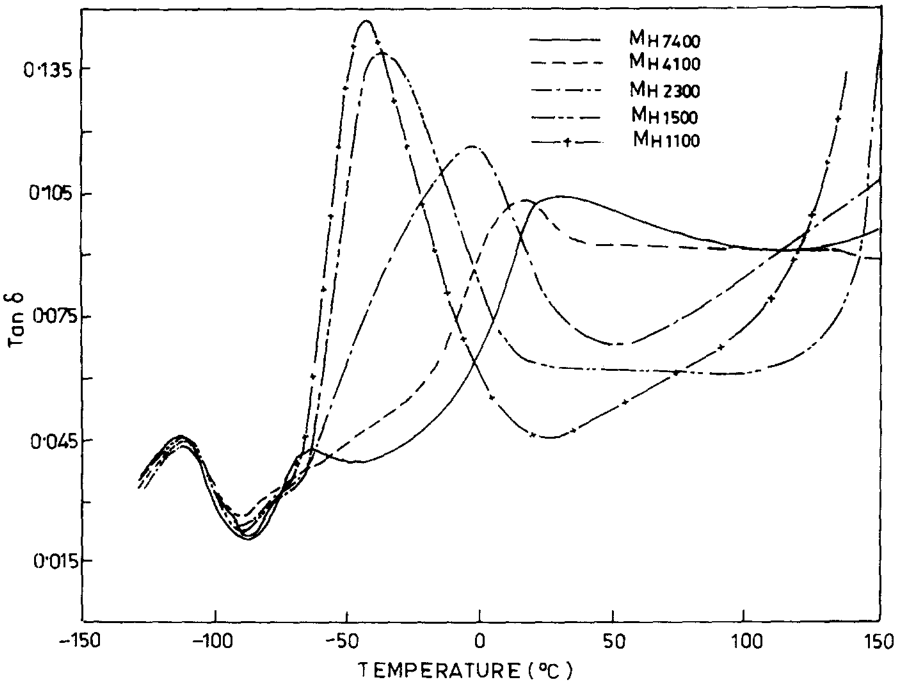

Figure 1 Effect of variations in the hard block molecular weight on the tan δ–temperature curve (M_n of PTHF = 1000) at a fixed frequency of 1 Hz

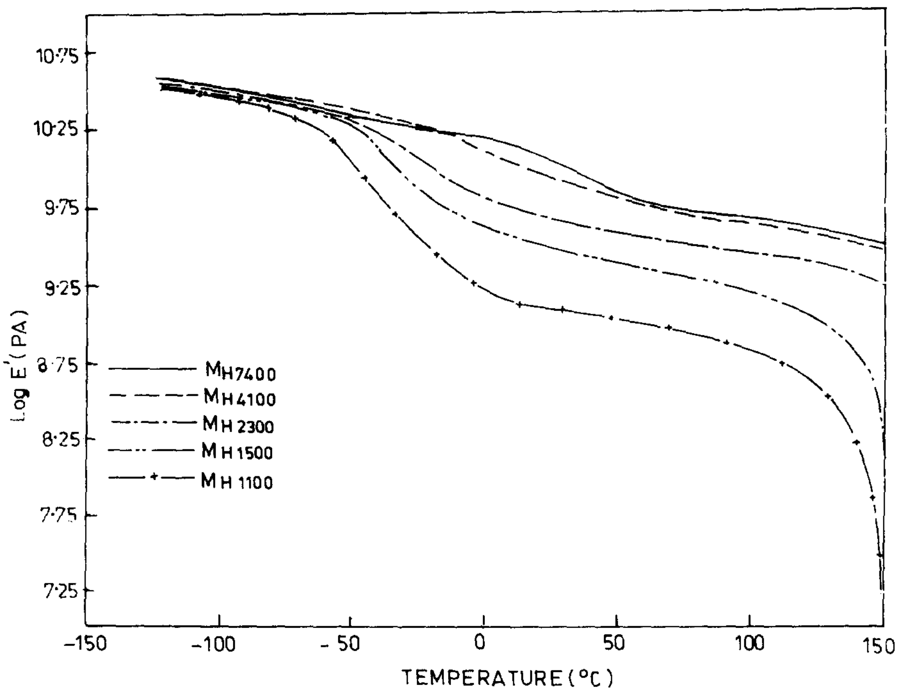

Figure 2 Effect of variations in the hard block molecular weight on the log E'–temperature curve (M_n of PTHF = 1000) at a fixed frequency of 1 Hz

Table 2 tan δ peak values and transition temperatures of various transitions for different Vestamid polymers

Sample	α transition		β transition		γ transition	
	tan δ peak value	Temp. (°C)	tan δ peak value	Temp. (°C)	tan σ peak value	Temp. (°C)
M_{H7400}	0.10	27	0.03	− 65	0.05	− 113
M_{H4100}	0.11	14	0.04	− 68	0.05	− 113
M_{H2300}	—	—	0.12	− 5	0.05	− 113
M_{H1500}	—	—	0.14	− 38	0.05	− 113
M_{H1100}	—	—	0.15	− 45	0.05	− 113
M_{S650}	—	—	0.14	− 32	0.05	− 112
M_{S1400}	—	—	0.13	− 47	0.05	− 112
M_{S2000}	—	—	0.12	− 47	0.05	− 112

nickel-filtered Cu Kα radiation from a Philips X-ray generator (type PW1729). Accelerating voltage and electron current were 40 kV and 20 mA, respectively. The range of 2θ value chosen for the study was 5–30°.

RESULTS AND DISCUSSION

Dynamic mechanical properties

The effect of variation of block molecular weight on the dynamic mechanical properties of segmented polyamides is illustrated in *Figures 1–5*.

Effect of molecular weight variation of hard block

Figures 1 and 2 indicate the effect of molecular weight variations in the polyamide hard block (molecular weights of hard segment are 7400, 4100, 2300, 1500 and 1100) at a constant molecular weight of PTHF soft segment (M_n = 1000). The presence of distinct dispersion regions due to the soft and hard blocks, as characterised by a drop in the modulus and accompanied by a peak in the loss tangent, is evident from these figures. The different dispersion regions are labelled as α, β and γ, descending from higher to lower temperatures, following the standard nomenclature for nylons[8–11]. The temperatures corresponding to the transitions are determined from *Figure 1* and reported in *Table 2*. For the M_{H7400} polymer having the highest hard block molecular weight, the dispersions are found to occur at +27, −65 and −113°C. The tan δ peak values corresponding to these transitions are 0.10, 0.03 and 0.05, respectively. The expected transition caused by the melting of the hard blocks is not shown in the figure.

The transition occurring at about +27°C, assigned to be the α transition, reflects the onset of motion of large chain segments caused by the breaking of intermolecular bridging in the amorphous region of the hard block. The β dispersion occurring at about −65°C is assumed to be a result of the simultaneous occurrence of two relaxations at this temperature, one caused by the relaxation of the soft amorphous polyether segments and the other caused by the local segmental motion of the amide groups in the amorphous region which are not hydrogen bonded to the other amide groups. Pechhold and Pruckmayr [12] reported a transition temperature near −60°*C* for polyether. Similarly, Kawaguchi [9] observed β transition for nylon near −50°*C*. The γ peak occurring at about −113°C is caused by the well-known crankshaft mechanism. This peak reflects the onset of co-operative movement of methylene groups in the amorphous region which are present in the polyether and polyamide segments.

In the series of polymers designated by M_{H7400}, M_{H4100}, M_{H2300}, M_{H1500} and M_{H1100}, the α peak gradually shifts to lower temperature and the tan δ peak height increases, as the hard block molecular weight decreases at a constant soft segment molecular weight of 1000. The β peak also becomes less conspicuous (*Figure 1*). The tan δ peak observed at −113°C for γ transition has a constant value of 0.05. The storage moduli (E') of the samples at different temperatures are plotted in *Figure 2*. Log E' has a value of 10.02 at 25°C in the case of M_{H7400} polymer. However, the log E' value decreases, as the molecular weight of the hard block decreases (*Table 3*). The hard polyamide blocks are mainly responsible for the modulus of the material and with

Table 3 Storage moduli of different Vestamid polymers at different temperatures

Sample	Log *E*′ (PA)		
	(− 113°C)	(25°C)	(140°C)
M_{H7400}	10.54	10.02	9.54
M_{H4100}	10.56	9.94	9.52
M_{H2300}	10.53	9.62	9.28
M_{H1500}	10.60	9.46	8.80
M_{H1100}	10.50	9.08	8.14
M_{S650}	10.60	9.52	8.72
M_{S1400}	10.62	9.20	8.34
M_{S2000}	10.70	9.10	7.36

Table 4 Crystallinity of different Vestamid polymers

Sample	% Crystallinity
M_{H7400}	22
M_{H4100}	20
M_{H2300}	18
M_{H1500}	14
M_{H1100}	09
M_{S650}	14
M_{S1400}	07
M_{S2000}	05

the decrease in the molecular weight of the hard block, the storage modulus is expected to decrease. In contrast, *E*′ value, near the temperature of the γ transition is of the same order in each case. The polymer exists in a glassy state at this temperature. However, log *E*′ value decreases, as the hard block gets softened at a temperature of 140°C, which is close to the melting point of these five polymers.

The α and β transitions occur distinctly and separately in the case of M_{H7400} and M_{H4100} polymers. But for the rest three polymers, namely M_{H2300}, M_{H1500} and M_{H1100}, the two transitions gradually merge together to give a single broad transition with the decrease in molecular weight of the hard block. There may be a second possibility for the occurrence of a single transition instead of two. The decrease in molecular weight of the hard block may result in an increased compatibility between the soft *amorphous* polyether phase and the hard *amorphous* polyamide phase. Thus a combined amorphous phase composed of polyether and polyamide may give rise to a single transition. This single transition occurs at −5, −38 and −45°C for the M_{H2300}, M_{H1500} and M_{H1100} polymers, respectively (*Figure 1*). The tan δ peak values are 0.12, 0.14 and 0.15, respectively. However, a small hump in the temperature range of −65 to −85°C occurs in each case due to the local segmental motion of the amide groups non-bonded to other amide groups. As the molecular weight of the hard segment is decreased, the number of polar amide groups per unit chain length is decreased. These amide groups are responsible for interchain hydrogen bonding, and as their number decreases, the extent of interchain hydrogen bonding also decreases leading to a decrease in structural symmetry of the polymers. Therefore, the crystallinity of the material decreases with decrease in molecular weight of the hard block, which has been confirmed from X-ray diffraction studies. The crystallinity is reduced from 22% for M_{H7400} sample to 9% for M_{H1100} sample (*Table 4*). The α peak shifts to lower temperature and the amount of damping also increases, because the restraints preventing the separation of the amide groups on adjacent chain decrease. The variation of tan δ peak values, Y_A (for β or $\alpha + \beta$ transitions) with the molecular weight of the hard block (x_1) is represented in *Figure 3* and described by a logarithmic equation:

$$Y_A = -0.07\ln(x_1) + 0.62 \qquad (2)$$

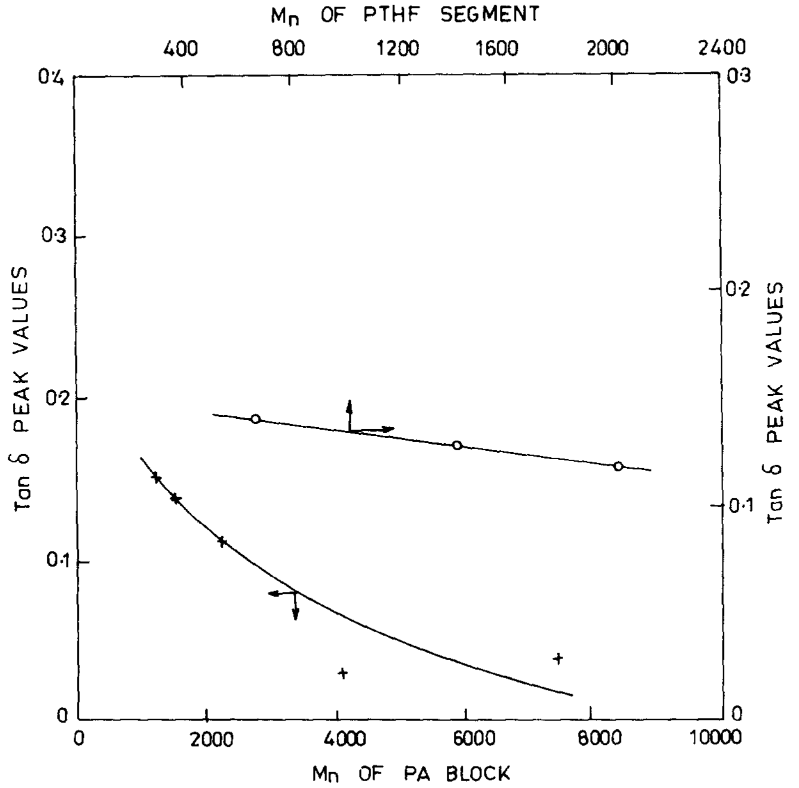

Figure 3 Variations of tan δ peak value (for β and $\alpha + \beta$ transitions) with hard and soft block molecular weight

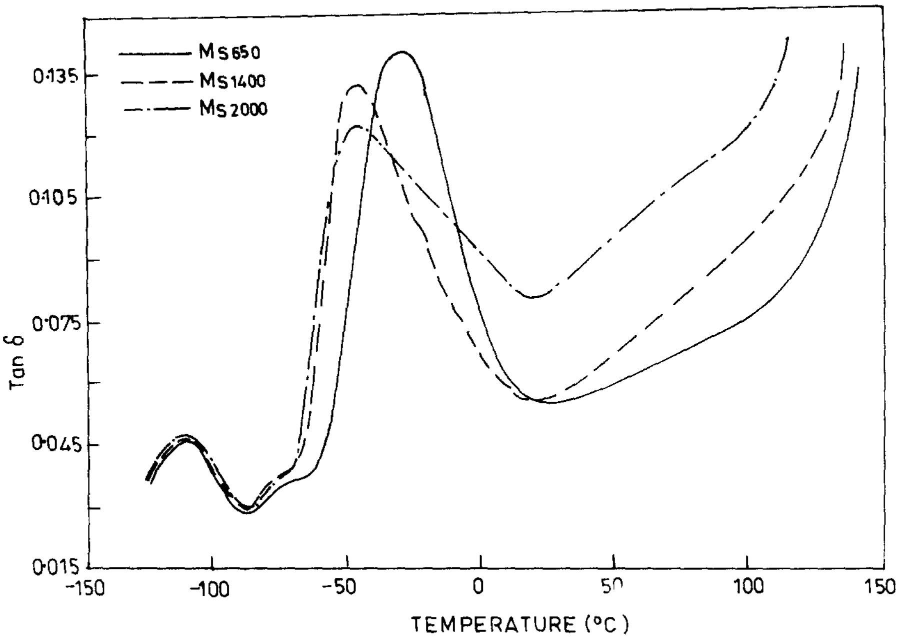

Figure 4 Effect of variations in the soft segment molecular weight on the tan δ-temperature curve (M_n of PA = 1100) at a fixed frequency of 1 Hz

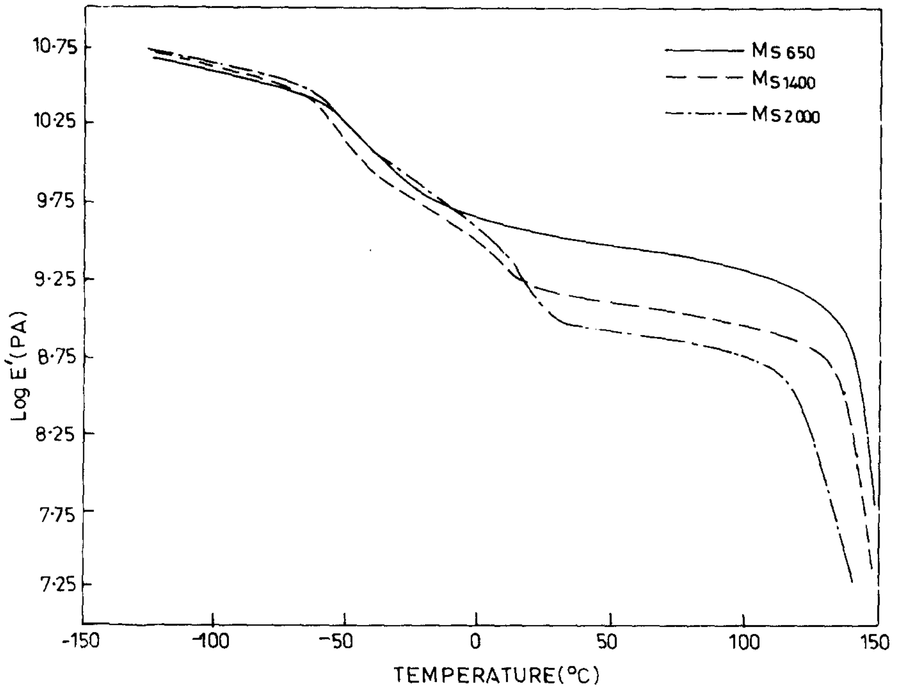

Figure 5 Effect of variations in the soft segment molecular weight on the log E'-temperature curve (M_n of PA = 1100) at a fixed frequency of 1 Hz

Effect of variation of soft segment molecular weight

Figures 4 and 5 describe the effect of variation in the soft segment molecular weight, at a constant hard block molecular weight, on the dynamic mechanical properties of segmented polyamide. In the series, M_{S650}, M_{S1400} and M_{S2000} polymers, the soft segment molecular weight increases at a constant hard block molecular weight of 1100. The α and β peaks merge together to give one single transition occurring at about −32, −47 and −47°C, respectively (*Figure 4*). The tan δ peak values are 0.14, 0.13 and 0.12, respectively (*Table 2*). A small hump occurs in the region of −65 to −85°C. The explanation for the occurrence of a single transition and the small hump is the same as given earlier. The peak due to the crankshaft mechanism involving $-(CH_2)_n-$ groups occurs at −112°C in each case, and the tan δ peak value remains constant at 0.05. Storage modulii of the samples at different temperatures are plotted in *Figure 5*. Log E' at 25°C has the highest value of 9.52 in the case of M_{S650} polymer, which has the lowest soft block molecular weight (*Table 3*). Log E' value, however, decreases with the increase in molecular weight of the soft segment because the material gets softer. E' value near the temperature region of γ transition is of the same order for all polymers, as the polymers exist in a glassy state at this temperature. The hard block softens at a temperature close to the melting of the hard block, resulting in a decrease of log E' values. It is observed from *Figure 4* that, as the molecular weight of the soft block increases, the tan δ peak

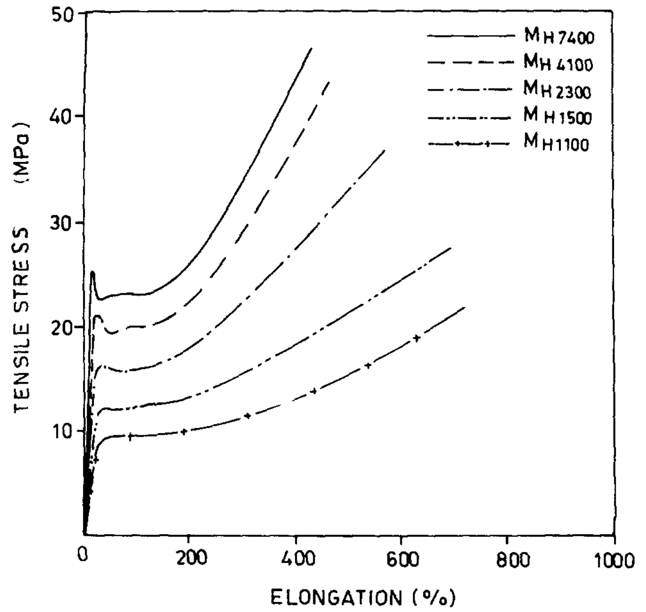

Figure 6 Stress–strain curves of M_{H7400}, M_{H4100}, M_{H2300}, M_{H1500} and M_{H1100} polymers

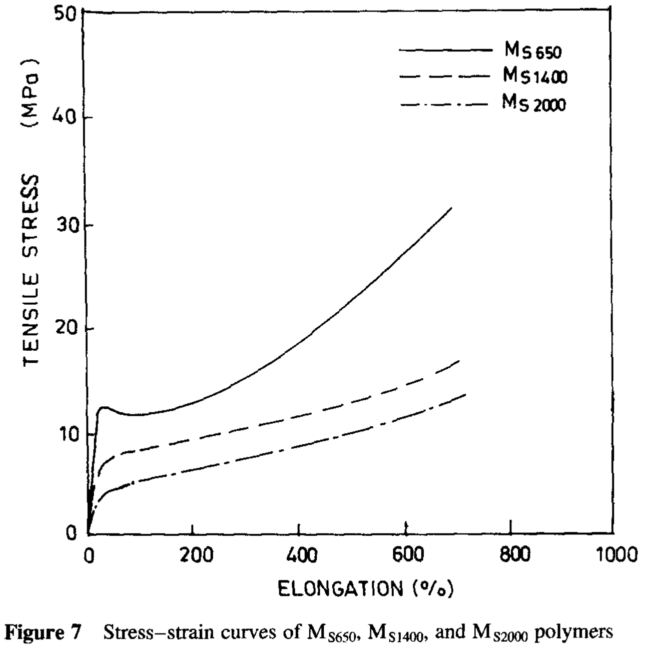

Figure 7 Stress–strain curves of M_{S650}, M_{S1400}, and M_{S2000} polymers

of the combined α and β transitions shifts to lower temperatures to some extent, but the magnitude of damping decreases. As the molecular weight of the polyether segments increases, the restrictive influence of the hard segment structures becomes less important and, accordingly, the glass transition of the polymer occurs at a lower temperature. On closer inspection, it is observed that though the loss modulus at the transition region increases, the storage modulus also increases. Thus, tan δ which is the ratio of loss modulus to the storage modulus decreases in magnitude. The increase in storage modulus indicates that the soft polyether segments interact to a greater extent as a result of increased dipolar attraction between the chains with the increase of soft segment molecular weight.

The tan δ peak values, Y_B, for the combined (α+β) transition decreases linearly with the soft segment molecular weight, x_2 (*Figure 3*) and is represented by the equation:

$$Y_B = 1.48 \times 10^{-5} x_2 + 0.15 \quad (3)$$

Mechanical properties

Figures 6 and 7 illustrate the variation of stress–strain properties with the change in molecular weight of the hard and soft segments. The results are reported in *Table 5*. In the series of polymers M_{H7400}, M_{H4100}, M_{H2300}, M_{H1500} and M_{H1100}, the M_{H7400} polymer has the highest hard block molecular weight. Accordingly, it exhibits the highest tensile strength, 300% modulus, yield stress and Young's modulus values of 46.0, 34.1, 25.6 and 157.6 MPa, respectively. These properties decrease with the decrease in molecular weight of the hard block (*Table 5*). The minimum tensile strength, 300% modulus, and Young's modulus values of 22.9, 11.5 and 32.9 MPa are observed in the case of M_{H1100} polymer, which has the lowest hard block molecular weight. The M_{H1500} and M_{H1100} polymers do not record any yield stress data. However, in this series, the elongation at break increases and attains the maximum value of 759% in the case of M_{H1100} polymer. The hard polyamide blocks are responsible for the good mechanical strength of the polymer and their decrease in molecular weight lowers the mechanical properties of the segmented polyamides. The crystallinity also decreases with decreasing hard block molecular weight (*Table 4*).

On the other hand, in the series of polymers M_{S650}, M_{S1400} and M_{S2000}, the M_{S650} polymer has the lowest soft segment molecular weight and exhibits the highest tensile strength (30.2 MPa), 300% modulus (15.4 MPa), yield stress (12.8 MPa) and Young's modulus (72.8 MPa) (*Table 5*). The tensile strength and 300% modulus decrease with

Table 5 Mechanical properties of different Vestamid polymers

Sample	TS (MPa)	EB (%)	100% modulus (MPa)	200% modulus (MPa)	300% modulus (MPa)	Set (%)	$W_1 \times 10^{-6}$ (J m^{-3})	H_R	Yield stress (MPa)	Young's modulus (MPa)
M_{H7400}	46.0	420	23.6	26.1	34.1	78	22.1	0.95	25.6	157.6
M_{H4100}	42.3	437	21.4	24.1	30.6	72	17.5	0.92	21.6	130.1
M_{H2300}	38.1	570	16.1	17.9	21.8	67	13.2	0.90	16.4	93.6
M_{H1500}	27.3	689	11.9	12.9	14.8	53	8.6	0.85	—	64.5
M_{H1100}	22.9	759	9.5	10.3	11.5	50	6.8	0.79	—	32.9
M_{S650}	30.2	696	12.3	13.1	15.4	69	10.2	0.88	12.8	72.8
M_{S1400}	15.9	710	7.9	8.7	9.6	40	4.8	0.77	—	34.7
M_{S2000}	13.1	700	5.3	6.2	7.3	35	3.4	0.74	—	26.1

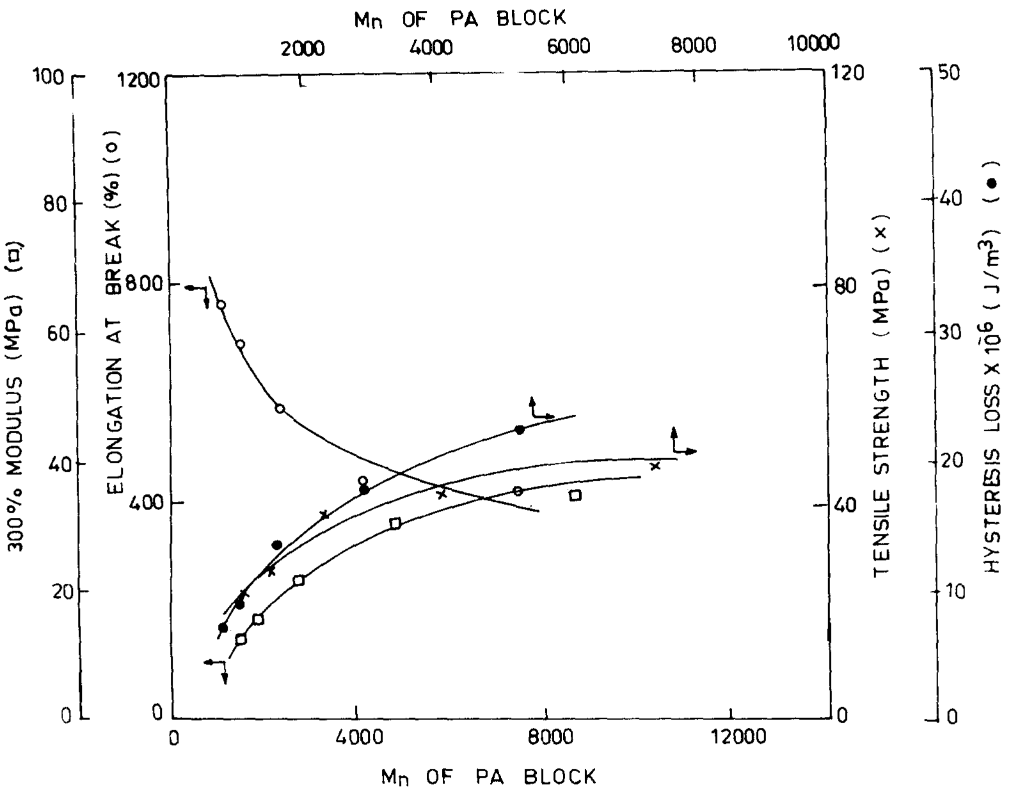

Figure 8 Variations of TS, EB%, 300% modulus and $W_1 \times 10^{-6}$ (J m^{-3}) with hard block molecular weight (M_n of PTHF = 1000)

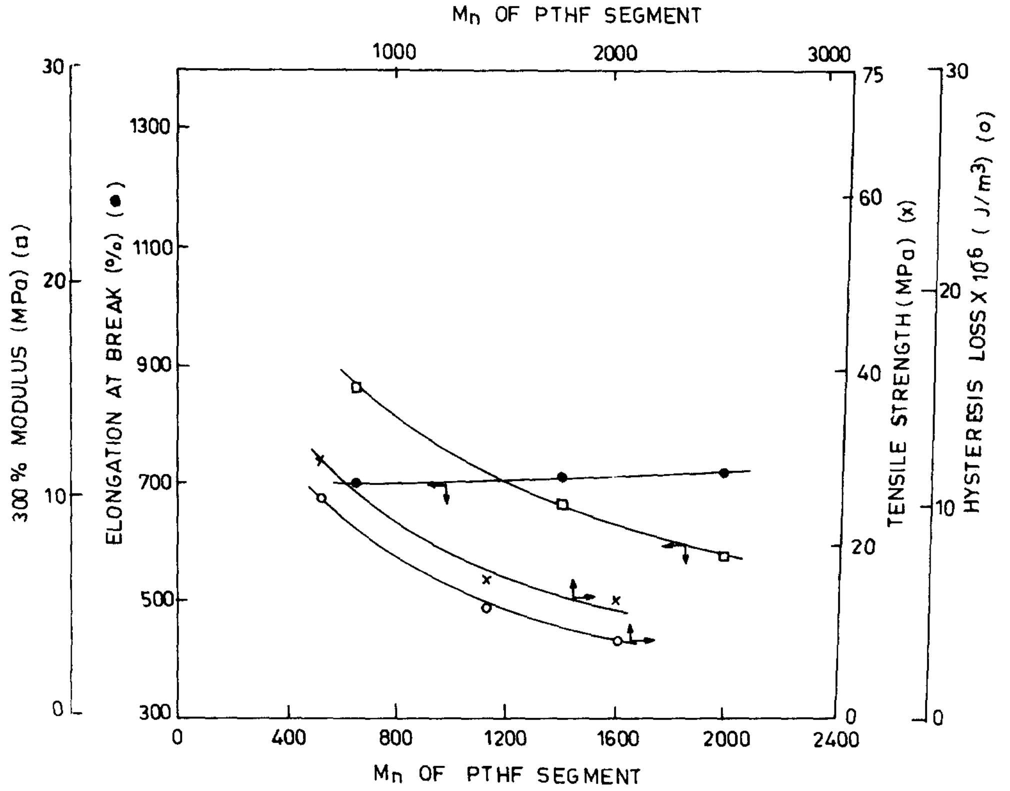

Figure 9 Variation of TS, EB%, 300% modulus and $W_1 \times 10^{-6}$ (J m^{-3}) with soft block molecular weight (M_n of PA = 1100)

increase in soft segment molecular weight and attain the minimum values of 13.1 and 7.3 MPa, respectively, for the polymer M_{H2000}, which has the highest soft segment molecular weight. However, M_{S1400} and M_{S2000} polymers do not record any yield stress data. The elongation at break remains almost the same in the series. Molecular weight increase in the soft segment of these three polymers makes them softer and results in reduced crystallinity, which leads to a fall in their mechanical strength.

It is interesting to note that the different mechanical properties vary differently with the molecular weights of the hard and soft blocks. The variations of the physical properties with the block molecular weight are represented in *Figures 8 and 9*, and given by the following equations:

$$y_1 = 12.34\ \ln(x_1) - 61.62 \tag{4}$$

variation of TS (y_1) with hard block molecular weight (x_1).

$$y_2 = -15.76\ \ln(x_2) + 131.74 \tag{5}$$

variation of TS (y_2) with soft block molecular weight (x_2).

$$y_3 = x_1^{-0.34} \times 7812.93 \tag{6}$$

variation of EB% (y_3) with hard block molecular weight (x_1).

$$y_4 = 0.0036x_2 + 697.13 \tag{7}$$

variation of EB% (y_4) with soft block molecular weight (x_2).

$$y_5 = 12.55\ \ln(x_1) - 76.06 \tag{8}$$

variation of 300% modulus (y_5) with hard block molecular weight (x_1).

$$y_6 = -7.26\ \ln(x_2) + 62.39 \tag{9}$$

variation of 300% modulus (y_6)with soft block molecular weight (x_2).

From the tensile stress–EB% curves, it can be noted that only the polymers M_{H7400}, M_{H4100}, M_{H2300} and M_{S650} exhibit the phenomena of yielding. It is observed from the figures that for all the polymers the stress initially rise in an approximately linear manner as the applied strain increases. The deformation is generally homogeneous in this region. At the yield point no increase in applied stress is required to increase the deformation further. However, as the yield point is reached, the stress begins to fall and rises less steeply with the strain. This is attributed due to the strain softening effect occurring in these polymers. In molecular terms, this strain is associated with some uncoiling and straightening of the hard polyamide chains. At this stage, it is thought that some slippage of polyamide chains past one another has occurred. Finally, at large extensions the slope of the stress–strain curves of these polymers increase because of the strain hardening effect.

At the yield point, an instability sets in and the specimen begins to neck down at some particular point as this region thins to a smaller cross-section than the rest of the material[3]. In the case of some polymeric materials, like M_{H7400} and M_{H4100}, this necked region soon stabilizes at some reduced diameter. Gradually the necked region propagates along the length of the sample. For rest of the materials there is no localised necking, but only a gradual uniform reduction in cross-sectional area is observed. After the yield point, however, the deformation resembles elastomeric deformation. Marked local deformation occurs in the vicinity of the necked region for the polymers exhibiting yield maximum. With the onset of necking, the local stress at the necked region rises because of the reduced cross-sectional area. As the polymer is strained and the neck is developing, the material in the vicinity of the necked region is being extensively deformed and the polyamide chains undergo conformational changes and marked reorientation. The strength and stiffness of the original necked region rise as the deformation proceeds. Further extension of the specimen occurs only by propagation of the neck along the specimen [13].

Only the M_{H7400} and M_{H4100} samples exhibit a cold draw after necking at room temperature and the deformation gradually increases after this. The initial ordered structure of the polymer is broken down and more and more of the hard polyamide chains become aligned in the drawn direction as cold drawing proceeds. Hence, both modulus and strength in this direction increase.

Hysteresis study

The hysteresis loss (W_1), hysteresis ratio (H_R) and set values of the segmented polyamides are reported in *Table 5*. The M_{H7400} polymer having the highest hard block molecular weight exhibits the highest hysteresis loss, hysteresis ratio and set values of 22.1 × 10^6 J m^{-3}, 0.95 and 78%, respectively. With decrease in molecular weight of hard block, these parameters decrease and attain the minimum values in the case of M_{H1100} polymer which has the lowest hard block molecular weight. The high set values of these polymers indicate their thermoplastic character. In the case of high hard block molecular weight polymers, like M_{H7400}, M_{H4100}, etc., the hysteresis loss is high, because of more energy dissipation and yielding.

On the other hand, the M_{S650} polymer having the lowest soft segment molecular weight, among the M_{S650}, M_{S1400} and M_{S2000} polymers, exhibit the highest set of 69%. The W_1 and H_R values are 16.2 × 10^6 J m^{-3} and 0.88, respectively. These values decrease with the increase of soft segment molecular weight. The set values are considerably lower in the case of M_{S1400} and M_{S2000} polymers having high soft segment molecular weight, indicating their predominant elastomeric behaviour. The variations of hysteresis loss and set values with the molecular weight of hard and soft segments are represented by the following equations:

$$y_7 = 8.19\ \ln(x_1) - 50.70 \tag{10}$$

variation of $W_1 \times 10^{-6}$ (J m^{-3}) (y_7) with hard block molecular weight (x_1) (*Figure 8*).

$$y_8 = -6.21\ \ln(x_2) + 50.25 \tag{11}$$

variation of $W_1 \times 10^{-6}$ (J m^{-3}) (y_8) with soft segment molecular weight (x_2) (*Figure 9*).

$$y_9 = 15.26\ \ln(x_1) - 55.95 \tag{12}$$

variation of % set (y_9) with hard block molecular weight (x_1).

$$y_{10} = -30.49\ \ln(x_2) + 265.42 \tag{13}$$

variation of % set (y_{10}) with soft segment molecular weight (x_2).

CONCLUSIONS

The effects of molecular weight variation in the hard and soft segments of segmented polyamide block copolymer have been studied.

(1) In the series of polymers M_{H7400}, M_{H4100}, M_{H2300}, M_{H1500} and M_{H1100}, the M_{H7400} and M_{H4100} polymers exhibit three peaks α, β and γ in the tan δ–temperature curve. For the other three polymers the α and β transitions merge to give a single transition. The damping increases and the ($\alpha + \beta$) transition temperature shifts to lower values. The M_{H7400} polymer has very high tensile strength, 300% modulus and hysteresis loss values of 46.0, 34.1 MPa and 22.1 × 10^6 J m^{-3}, respectively. These parameters decrease on decreasing hard block molecular weight. The elongation at break, however, increases in this series.

(2) Similarly in the case of M_{S650}, M_{S1400} and M_{S2000} polymers, the α and β transitions couple together to give a single transition. This combined ($\alpha + \beta$) transition temperature shifts to a lower value, but the tan δ peak value decreases due to an increase in storage modulus value at the transition temperature and increased dipolar interaction of the polyether segments. The M_{S650} polymer records the highest tensile strength, 300% modulus and hysteresis loss values of 30.2, 15.4 MPa and $10.2 \times 10^6\,J\,m^{-3}$, respectively. These parameters decrease on increasing soft block molecular weight. The elongation at break, however, remain almost the same in this series.

(3) These segmented polyamides, except the M_{S1500}, M_{H1100}, M_{S1400} and M_{S20000} polymers, exhibit the phenomenon of yielding. Only the M_{H7400} and M_{H4100} polymers show a neck after yield and subsequent cold draw. Barring the M_{S1400} and M_{S2000} polymers, the other six polymers show high set values, thus indicating their thermoplastic nature. The M_{S1400} and M_{S2000} are predominantly elastomeric in character.

(4) Decrease in molecular weight of hard block or increase in molecular weight of soft segment results in a decreased crystallinity of the different segmented polyamides.

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