Melt Rheology of Segmented Polyamides: Effect of Block Molecular Weight

SUBIMAN GHOSH, ASISH K. BHATTACHARYYA, DIPAK KHASTGIR, ANIL K. BHOWMICK

Rubber Technology Centre, Indian Institute of Technology, Kharagpur, 721 302, India

Received 11 March 1998; accepted 23 April 1998

ABSTRACT: Segmented polyamides, also known as polyether-ester-amides, are composed of polyether and polyamide structural units. The rheological behavior of segmented polyamides with respect to the variations in the molecular weight of hard and soft blocks has been studied using a Monsanto Processability Tester. These systems exhibit pseudoplastic flow behavior. The shear viscosity of the segmented polyamides decreases with a decrease in hard block molecular weight up to 1500. However, at low shear rates, the shear viscosity shows marginal change with an increase in soft segment molecular weight. The equilibrium die swell increases with an increase in shear rate, but decreases with increasing temperature. The stress relaxation study of the segmented polyamides reveals that the stress developed during extrusion relaxes exponentially for all the systems. The equilibrium die swell at a fixed temperature and shear rate, the time required to relax a fixed amount of stress and the stress developed after a certain time interval decrease with a decrease in hard block molecular weight up to 1500, but increase with an increase in soft segment molecular weight. The activation energy of the melt flow process increases with the rate of shear in most of the cases. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1739-1747, 1999

Key words: melt rheology; segmented polyamides; block molecular weight

INTRODUCTION

A block copolymer in bulk often forms a microphase separated structure, which is primarily a characteristic of its molecular weight, composition, and processing conditions.^{1–3} Because of the industrial importance of block copolymers, a larger number of studies have been carried out, especially on styrene–butadiene block copolymers.^{4,5} Another interesting example of block copolymers 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"

Correspondence to: A. K. Bhowmick.

Journal of Applied Polymer Science, Vol. 71, 1739–1747 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/111739-09 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 (tetramethyleneether) glycol segments. Because the structural units are linked via an ester group, such systems are also referred to as polyetherester amides⁶ having the chain structure as shown below:



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 mean 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 intraas well as intermolecular hydrogen bonding, 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 processing of a polymer is an important operation in the manufacture of goods made from them and the various steps of polymer processing generally involve various flow states. The prediction of performance and control of a particular processing step requires the knowledge of both the viscous and elastic properties of the polymer compounds. The viscous behavior at different conditions determines the output, whereas the elastic properties are important for dimensional stability. A number of reviews are available on processability and relevant rheological properties of various polymer melts.^{7,8} The rheological behavior has been reported to vary in general with the nature of the polymer, temperature, 9,10 molecular weight, and its distribution.^{11,12} Prior to this study, Parrini et al.¹³ studied the melt rheology of nylon-6, nylon-6,6, nylon-6,10, and nylon-11. Pezzin¹⁴ investigated the capillary viscometry of molten caprolactum only. Melt rheology of nylons with reference to moisture and molecular weight variation has been reported.¹⁵ Effects of molecular weight and block length ratio of styrene-isoprene-styrene block copolymers on the rheological behavior in the disordered state have been highlighted.¹⁶ There are also reports on the rheological features of a few block copolymeric systems.^{17–19} The technological properties of a few commercial Vestamid polymers have also been discussed.²⁰ However, from the review of literature, it is revealed that there is no study in understanding the influence of structure and molecular weight on the melt rheology of segmented polyamides.

The objective of this article is to investigate the processability of the segmented polyamides at

various shear rates and temperatures. Systematic variations have been made in the molecular weight of the hard and soft segments. The viscoelastic properties of these materials have been correlated with the molecular weight of the hard and soft segments.

EXPERIMENTAL

Materials Used

Vestamid polymers with specific gravity in the range of 1.01–1.02 and different shore-D hardness were provided by Dr. J. Lohmar of HÜLS, AG, Germany. Molecular weight (M_n) variations were made in the hard and soft blocks. Table I lists the M_n of PTHF and PA segments, melting point, and hardness of the Vestamid polymers used in this investigation. The total molecular weight of the samples estimated by the terminal group titration was between 22,000–26,000, which means that n/2 in the structure shown is between 3.5–5.0, respectively.

Measurement of Processability

The processability was measured using a Monsanto Processability Tester, which is a microprocessorbased automated and programmable capillary rheometer. The measurement was carried out using a capillary having a length-to-diameter ratio of 30:1with compound entrance angles of 45° and 60° . The extrusion studies were carried out at three different temperatures, viz., 190, 200, and 210°C and at four different shear rates of 61.45 s^{-1} , 122.90 s⁻¹, 245.81 s⁻¹, and 1229.04 s⁻¹.

Wall shear stress, τ_w , wall shear rate, $\dot{\gamma}_w$, and shear viscosity, η , were calculated using the following equations:

$$\tau_w = d_c \Delta P / 4\ell_c \tag{1}$$

$$\dot{\gamma}_{w,a} = 32Q/\pi d_c^3 \tag{2}$$

$$\dot{\gamma}_w = \frac{(3n'+1)}{4n'} \times \dot{\gamma}_{w,a} \tag{3}$$

$$\eta = \tau_w / \dot{\gamma}_w \tag{4}$$

Here, ΔP is the pressure drop across the length of the capillary, d_c and ℓ_c are the diameter (1 mm) and length of the capillary (30 mm), respectively. $n' = d \log \tau_w/d \log \dot{\gamma}_{w,a}, Q$ is the volumetric flow

Samples	DSC Melting Point (°C)	Shore D Hardness	PTHF Segment		PA Segment	
			M_n	x	M_n	$y_1 + y_2$
$M_{H7400^{b}}$	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

Table I M_n of PTHF and PA Segments, Hardness, and Melting Point of Different Segmented Polyamides^a

^a In the structure shown in the Introduction, k = 4 (polytetrahydrofuran); l = 11 (laurolactum); m = 12 (dodecanoic acid); n = 7-10; x indicates the length of the soft block, while $y_1 + y_2$ indicates the length of the hard block. The total molecular weight of the samples estimated by the terminal group titration was between 22,000–26,000. ^b Here $M_{\rm H}$ denotes variation of hard block molecular weight at a constant soft-segment molecular weight of 1000. But $M_{\rm S}$

^b Here $M_{\rm H}$ denotes variation of hard block molecular weight at a constant soft-segment molecular weight of 1000. But $M_{\rm S}$ 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 $M_{\rm H}$ of $M_{\rm S}$ denotes the corresponding hard block or soft-segment molecular weight.

rate, and $\dot{\gamma}_{w,a}$ is the apparent wall shear rate. n' is determined from the slope of the line obtained by plotting log τ_w vs. log $\dot{\gamma}_{w,a}$ and n' = n (flow behavior index) when n' remains constant for the range of shear rates studied. Because the capillary having a large length-to-diameter ratio of 30 : 1 was used, the Bagley correction for shear stress is negligible, and hence, the values of shear stress obtained are taken as the true shear stress values.²¹

The extrudates coming out of the capillary were collected for measurement of equilibrium die swell, taking maximum care to avoid any further deformation. The diameter of the extrudate was measured after equilibrium was reached. For measuring the diameter of an extrudate, a fixed length of the uniform portion of the extrudate was cut, and its weight was taken as accurately as possible. The diameter of the extrudates was then calculated by using the following relation:

Volume of the extrudate
$$(V) = \frac{\pi d_e^2}{4} \cdot \ell_e$$
 (5)

Density
$$(D) = M/V$$
 (6)

$$\therefore D = \frac{M}{\frac{\pi d_e^2}{4} \cdot \ell_e} \tag{7}$$

$$\therefore d_e = \left(\frac{4M}{\pi \ell_e D}\right)^{1/2} \tag{8}$$

where ℓ_e , M, and d_e are the length, mass, and diameter of the extrudate, respectively.

The equilibrium die swell was determined by using the following relation:

Equilibrium die swell (α)

$$= \frac{\text{diameter of the extrudate } (d_e)}{\text{diameter of the capillary } (d_c)} \quad (9)$$

Measurement of Stress Relaxation Time

The stress relaxation experiments were performed in the Monsanto Processability Tester by allowing the piston to move up to a certain length quickly and then stopping it suddenly. The maximum pressure developed just at the time of stopping the piston, and the time for relaxing a fixed percentage of this pressure were recorded automatically. In this way, the relaxation times over a range of 0 to 90% stress relaxation were recorded.

Activation Energy of Melt Flow

Activation energy of melt flow process at a constant rate of shear, E_{γ} , was determined by using the Arrhenius-Frenkel-Eyring formula²²:

$$\eta_{\dot{\gamma}} = B \exp\left(E_{\dot{\gamma}}/RT\right) \tag{10}$$

where $\eta_{\dot{\gamma}}$ is the viscosity at a particular shear rate, *B*, a constant, *R*, the gas constant, and *T*, the absolute temperature.



Figure 1 Viscosity as a function of shear stress and shear rate at 190°C for M_{H7400} , M_{H4100} , M_{H2300} , M_{H1500} , and M_{H1100} polymers (M_n of PTHF segment = 1000).

X-ray Studies

X-ray studies of the samples were performed with Phillips X-ray Diffractometer (Type PW 1340) using a nickel filtered CuK_{α} radiation from Phillips X-ray generator (Type PW 1729). Accelerating voltage and electron current were 40 kW and 20 mA, respectively. The range of 2 θ values chosen for the study was 5–30°.

RESULTS AND DISCUSSION

Viscous Effects in Melt Flow

The effects of molecular weight variation in the hard and soft blocks on the viscosity of the segmented polyamides at various shear stresses and shear rates at 190°C are shown in Figures 1 and 2. In all the cases, the viscosity decreases with increasing shear stress showing a pseudoplastic nature of the polymer. The flow behavior index, n, for all the segmented polyamides at different temperatures are presented in Table II.

In the series of polymers $M_{\rm H7400}$, $M_{\rm H4100}$, $M_{\rm H2300}$, $M_{\rm H1500}$, and $M_{\rm H1100}$, the hard-block mo-



Figure 2 Viscosity as a function of shear stress and shear rate at 190°C for M_{S650} , M_{S1400} , and M_{S2000} polymers (M_n of PA block = 1100).

lecular weight decreases at a constant soft-segment molecular weight of 1000. It is evident from Figure 1 that as the hard-block molecular weight decreases, the viscosity of the segmented polyamides decreases. However, it is interesting to note that for the polymer $\mathrm{M}_{\mathrm{H1100}},$ with the lowest hard-block molecular weight, the viscosity increases instead of decreasing in the initial stage. It can be said that as the molecular weight of the hard segment is decreased, the number of polar amide group 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 the decrease in the structural symmetry of the polymers.

Table IIFlow Behavior Index, n, of theDifferent Segmented Polyamides at DifferentTemperatures

=			
Samples	190°C	200°C	210°C
M _{H7400}	0.57	0.65	0.63
M_{H4100}	0.63	0.57	0.63
M _{H2300}	0.63	0.60	0.57
M_{H1500}	0.70	0.67	0.67
M_{H1100}	0.67	0.70	0.70
M ₈₆₅₀	0.70	0.70	0.73
M_{S1400}	0.63	0.63	0.67
M _{S2000}	0.67	0.63	0.63

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Samples	% Crystallinity			
M _{H7400}	22			
M_{H4100}	20			
M _{H2300}	18			
M _{H1500}	14			
M _{H1100}	9			
M _{S650}	14			
M _{S1400}	7			
M _{S2000}	5			

This is manifested in the decrease of crystallinity of the material with a decrease in hardblock molecular weight as confirmed from X-ray studies. The crystallinity is reduced from 22% for $M_{\rm H7400}$ polymer to 9% for $M_{\rm H1100}$ polymer (Table III). Therefore, the restraints preventing the separation of the amide groups on adjacent chains decrease, leading to an increased mobility of the polymer chains. This then accounts for the reduction in shear viscosity with hard-block molecular weight. Alternately, with decrease in hard-block molecular weight, the number of polyamide chain ends may increase, leading to an increase in the free volume of the segmented polyamides. This may also account for the reduction in viscosity.

As we go from $M_{\rm H1500}$ polymer to $M_{\rm H1100}$ polymer, the hard-block molecular weight decreases from 1500 to 1100, but curiously enough, the viscosity increases. It is possible that with a relative increase in the proportion of the flexible polyether chain segment, entanglement and coiling of the polymer molecules may take place in addition to the increased dipolar interaction between the polyether segments, thus leading to a rise in shear viscosity values.

On the other hand, for the group of polymers M_{S650} , M_{S1400} , and M_{S2000} , the soft-segment molecular weight increases at a constant hard-block molecular weight of 1100. From Figure 2, it is revealed that the viscosity of these three polymers does not vary much at low shear rates. However, at the highest shear rate of 1229.04 s⁻¹, the viscosity of the M_{S1400} and M_{S2000} polymers decreases marginally when compared with the viscosity of the M_{S650} polymer having the lowest soft-block molecular weight. As reported in our earlier article,²³ the dynamic mechanical analysis of these polymers reveal that the combined α and β transition temperature decreases with an in-

crease in soft-segment molecular weight. This decrease is associated with an increase in the free volume of the polymers. Consequently, the shear viscosity decreases with an increase in free volume.

Elastic Effects in Melt Flow

Equilibrium Die Swell—Effect of Rate of Shear and Block Molecular Weight

The variations of the equilibrium die swell with the rate of shear and block molecular weight are depicted in Figures 3 and 4. It is observed that the die swell, at a particular temperature and fixed shear rate, decreases with a decrease in hardblock molecular weight up to 1500, but increases with an increase in the soft-segment molecular weight. The results could be explained on the basis of interaction between the polyamide segments and that between the polyether segments, as discussed in an earlier section.

In the series of polymers, $M_{\rm H7400}$, $M_{\rm H4100}$, $M_{\rm H2300}$, $M_{\rm H1500}$, and $M_{\rm H1100}$, the die swell increases with an increase in the rate of shear (Fig. 3). The increase in die swell with increasing shear rate may be attributed to the considerable increase in the recoverable elastic energy of the system at higher shear rates.²⁴

Similarly, for the $M_{\rm S650},~M_{\rm S1400},$ and $M_{\rm S2000}$ polymers, the die swell increases with increasing



Figure 3 Equilibrium die swell as a function of shear rate and hard block molecular weight at 200°C (M_n of PTHF segment = 1000).



Figure 4 Equilibrium die swell as a function of shear rate and soft segment molecular weight at 200°C (M_n of PA block = 1100).

rate of shear, as shown in Figure 4. It is interesting to note that the M_{S2000} polymer having the highest soft-segment molecular weight, shows the maximum die swell in the range of shear rates studied. The explanation for the increase in die swell with the increasing rate of shear is the same as given above.

Equilibrium Die Swell—Effect of Temperature

The equilibrium die swell of the segmented polyamides, irrespective of the molecular weight variations in the hard and soft blocks, decreases with an increase in temperature, as shown in Figures 5 and 6. As the temperature increases, mobility of the polymer chain increases, which reduces the capacity of the polymer molecules to store the elastic energy, and hence, there is a reduction in the die swell values.

Stress Relaxation

The stress relaxation behavior of the segmented polyamides have been studied, and a few representative plots are shown in Figure 7(a) and 7(b). Molecular weight variations in the hard and soft blocks give rise to identical stress relaxation curves. The stress relaxation behavior of an elastomer can give an idea about the frozen-in strains in a system after processing. For all the segmented polyamides, it is observed that the stress decays exponentially with time. The time re-



Figure 5 Dependence of equilibrium die swell on temperature at $\dot{\gamma}_{w,a} = 1229.04 \text{ s}^{-1}$ for M_{H7400}, M_{H4100}, M_{H2300}, M_{H1500}, and M_{H1100} polymers (M_n of PTHF segment = 1000).

quired to relax a certain amount of stress and the stress developed after a certain time interval, obtained from the individual curve of the segmented polyamides at 200°C, are given in Table IV. Initially, there is a sharp fall in the stress followed by a slow relaxation process. The initial fast relaxation process may be due to a very low elastic



Figure 6 Dependence of equilibrium die swell on temperature at $\dot{\gamma}_{w,a} = 1229.04 \text{ s}^{-1}$ for M_{S650}, M_{S1400}, and M_{S2000} polymers (M_n of PA block = 1100).



Figure 7 Stress relaxation behavior of (a) $M_{\rm H2300}$ and $M_{\rm H1500}$ polymers and (b) $M_{\rm S1400}$ and $M_{\rm S2000}$ polymers at 200°C.

memory of these segmented polyamides. The almost asymmetric nature of the plots at higher times is due to the basic nature of the relaxation process according to which these systems take a very long time to come to an equilibrium, i.e., due to the configurational adjustment of the poly-

Table IVStress Relaxation Times and theStresses Developed for Different SegmentedPolyamides at 200°C

Samples	Time in (s) Required for 50% Stress Relaxation, i.e., for a Drop in Stress from 2.07×10^7 Pa to 1.03×10^7 Pa	Stress Developed after 30 s, Pa
Muzza	45	1.5×10^{7}
M ₁₁₄₁₀₀	15	$4.8 imes 10^6$
M _{H2300}	12	$4.1 imes10^6$
M_{H1500}	3	$6.8 imes10^5$
M _{H1100}	4.5	$6.9 imes10^5$
M _{S650}	_	_
M _{S1400}	3	$4.1 imes10^5$
M _{S2000}	4.5	$6.8 imes10^5$



Figure 8 Log viscosity vs. 1/T plot for $M_{\rm H7400}$ polymer at four different shear rates.

amide and polyether molecular segments.²² From the stress relaxation curves, it is seen that the initial stress developed in all the segmented polyamides is different. Therefore, to study the effect of block molecular weight on the stress relaxation times, the time corresponding to a certain drop in stress, i.e., from 2.07×10^7 Pa to 1.03×10^7 Pa (50% stress relaxation) was calculated from the curve of the individual polymers. The amount of stress developed, after a fixed time interval of 30 s, in the different segmented polyamides, was also calculated from the same stress relaxation curves. It is observed from Table IV that the 50% stress relaxation time and the stress developed after 30 s decrease with a decrease in hard-block molecular weight up to 1500, and with a decrease in soft-segment molecular weight, thus indicating that the elastic recovery of the polymer matrix goes on decreasing in each case. No stress relaxation data could be obtained for M_{S650} polymer as it exhibited liquid like flow.

Activation Energy of Melt Flow—Effect of Rate of Shear and Block Molecular Weight

Log η_{γ} has been plotted against 1/T for all the segmented polyamides. A representative plot for the $M_{\rm H7400}$ polymer at different shear rates is shown in Figure 8. The activation energy, E_{γ} of



Figure 9 (a) Activation energy of melt flow as a function of shear rate and hard block molecular weight $(M_n$ of PTHF segment = 1000). (b) Activation energy of melt flow as a function of shear rate and soft segment molecular weight $(M_n$ of PA block = 1100).

the melt flow process at a particular shear rate has been calculated from the slope of these plots following eq. (10). Figure 9(a) and 9(b) shows the dependence of activation energy on the rate of shear and block molecular weight. It is clear that within the given range of shear rates (61.45 s^{-1} - 1229.04 s^{-1}), the activation energy of viscous flow for the different segmented polyamides is found to be of the order of 14.7-10.9 kcal/mol. It is interesting to note that the activation energy increases with increase in shear rate for M_{H4100} , M_{H2300} , and $M_{\rm H1500}$ polymers, whereas the same decreases with increasing shear rate for the $M_{\rm H7400},$ M_{S650}, and M_{S1400} polymers. These polymers report an increase or a decrease in the activation energies with shear rates for various reasons. An increase in the value of activation energy with increasing shear rate may be due to the fact that the polymer matrix is subjected to higher deformation rate and, correspondingly, higher shear stress, thus requiring a higher energy for deformation. Decrease in the value of activation energy with an increase in shear rate results from the reduced energy needed for flow, possibly due to increased wall slip.¹⁰

CONCLUSIONS

The influence of molecular weight variation in the hard and soft blocks on the rheological behavior of segmented polyamides has been studied by using a Monsanto Processability Tester. These systems exhibit pseudoplastic behavior.

- 1. The shear viscosity of the segmented polyamides decreases with increasing shear stress. An increase in soft-segment molecular weight or a decrease in hard-block molecular weight up to 1500 decreases the shear viscosity in general.
- 2. The equilibrium die swell of the systems studied increases with an increase in shear rate, but decreases with an increase in temperature. The die swell at a fixed temperature and shear rate decreases with a decrease in hard-block molecular weight up to 1500 and increases with an increase in soft-segment molecular weight.
- 3. The stress relaxation study of the segmented polyamides reveals that the time required to relax a fixed amount of stress (i.e., from 2.07×10^7 Pa to 1.03×10^7 Pa) and the stress developed after a time interval of 30 s decrease with a decrease in hard-block molecular weight up to 1500, but increase with an increase in soft-segment molecular weight.
- 4. The activation energy of the melt flow process for the segmented polyamides in general, increases with the increase in shear rate. However, for $M_{\rm H7400}$, $M_{\rm S650}$, and $M_{\rm S1400}$ polymers, the $E_{\dot{\gamma}}$ values decrease with increasing shear rate.

The authors gratefully acknowledge the assistance put forward by Dr. J. Lohmar of HÜLS AG, Germany for providing the *Vestamid* samples used in our research work.

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