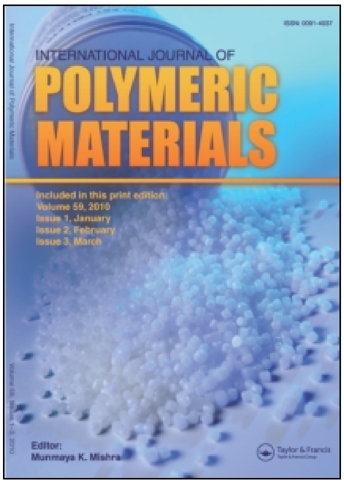

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Schnoor, M. , Kronewald, P. , Friedrich, K. , Evstatiev, M. and Fakirov, S.(2000) 'Effects of Molecular Weight and Thermal Treatment on Wear Behavior of Polyamide 6', International Journal of Polymeric Materials, 46: 1, 361 — 376

To link to this Article: DOI: 10.1080/00914030008054867

URL: http://dx.doi.org/10.1080/00914030008054867

Intern. J. Polymeric Mater., 2000, Vol. 46, pp. 361 – 376
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Effects of Molecular Weight and Thermal Treatment on Wear Behavior of Polyamide 6

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(Received 2 January 1999)

A series of polyamide 6 (PA 6) samples varying in their molecular weight (between 10 000 and 50 000) were annealed for 6 h in vacuum at various temperature (between 100 and 220°C) in order to create different morphological structures. The samples have been characterized with respect of their density, melting and crystallinity (from DSC), thermal expansion coefficient, humidity, predomination α- or γ-crystalline modification (from IR), shear melt viscosity and their tribological behaviour (the specific wear rate $\dot{W}_s$). It is found that density increases with increasing annealing temperature T_a but decrease with the rise of molecular weight (m.w.). The thermal expansion coefficient is more sensitive to T_a than to m.w. Contrary, shear-viscosity increases from 35 MPa for PA 6 with a m.w. of 10 000 to 7 200 MPa for samples with a m.w. of 50 000. Concerning wear behavior it is concluded that the observed tendency for a decrease of $\dot{W}_s$ with an increase of T_a, particularly for samples with low m.w. is attributed to the formation of a more stable physical structure during annealed. This well defined tendency (except samples annealing at highest T_a) is related to the observed drastic increase of shear melt viscosity with an increase of m.w.

Keywords: Polyamide 6; thermal treatment; molecular weight; density; crystallinity; thermal expansion coefficient; morphology; shear viscosity; specific wear rate

1. INTRODUCTION

The demand for polymeric materials with competitive and new properties for various applications is increasing steadily. A good wear

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resistance is an important requirement for engineering plastics in many cases. It is well known that the wear phenomenon is rather complex with respect to both, the mechanisms as well as the determining factors [1], *e.g.*, type and course of movement, normal force, sliding velocity, temperature and loading duration. The four basic mechanisms of wear are adhesion, abrasion, surface fatigue and tribochemical reactions [2]. Material characteristics also affect the wear behavior of polymers. In particular, the molecular weight should be of primary importance, since it determines viscous and viscoelastic properties of the materials as well as their crystallizability, that in turn affects the hardness of the surface and the bulk. Polyamide 6 (PA 6), one of the most common engineering plastics, has some pecularities in contrast to other polymers. First of all it absorbs a relative high amount of water (up to 10%); the latter can act as a plasticizer and decrease the glass transition temperature T_g strongly (down to 20–25°C). Further, fiber grade PA 6 has usually a molecular weight of 20 000–25 000 and a melt viscosity not high enough to be processed *via* injection moulding and extrusion. The proper viscosities for those processing techniques correspond to molecular weights of 30 000–40 000 and 50 000–70 000, respectively. It is worth to be mentioned here, that an increase of molecular weight from 20000 or below to around 30 000 results in a significant increase of tensile strength [3]. One could expect that such a change in molecular weight would also have a strong effect on the wear behavior of PA 6. This study aims to illustrate the effect of molecular weight of PA 6 in a range between 10 000 and 50 000 on its sliding wear characteristics against a steel counterpart.

2. EXPERIMENTAL

2.1. Materials

The starting material was a commercial PA 6 of type Vidlon (Chemical plant Vidin, Bulgaria). This freshly produced polymer had a molecular weight of 29 000 and was used to obtain samples with higher molecular weights through solid state post condensation [4, 5]. In addition, a recycled material with a lower molecular weight of 19 500 was selected for producing samples with lower molecular weights by solid state hydrolysis with formic acid as described in detail in [5]. The determination of their molecular weights took place by viscosimetric measurements. From the materials differing in their $\bar{M}_v$, "dog-bone" test samples were produced by injection moulding. In order to have the specimens not only differ in their molecular weights but also in their morphological structure, a subsequent thermal treatment was carried out in vacuum at various temperatures for 6 h. Details on all these procedures can be found in [5]. The molecular weights after the respective treatments together with the corresponding sample designation are given in Table I.

2.2. Morphological Characterization

Before starting the tribological measurements, the samples (Tab. I) were characterized with respect to their density ρ, melting temperature T_m, melting enthalpy ΔH, respectively degree of crystallinity X_c, thermal expansion coefficient α, humidity Δh, amount of α-or γ-crystalline modification, and shear viscosity η.

The density ρ has been determined by picnometric measurements at 20°C using deionized water:

$$\rho = \frac{F_a}{F_a - F_l} \cdot \rho_l \tag{1}$$

TABLE I Viscosimetric molecular weights $\bar{M}_v$ after respective treatment of PA 6 and sample designation

Sample group	*Starting molecular weight* [*g/mol*]	*Sample designation and molecular weight* [*g/mol*]					
		After injection moulding	*After* 6 *h annealing temperature* T_a				
			100° *C*	140° *C*	160° *C*	200° *C*	220° *C*
A		A1	A2		A4	A5	A6
	11 400	9600	9400		8700	7600	8400
B		B1	B2		B4	B5	B6
	19 500	17800	17600		17200	14800	17000
C		C1	C2	C3		C5	C6
	29 000	27000	28500	28600		35500	51000
D		D1	D2		D4	D5	D6
	39 500	33600	33800		34700	41400	47400
E		E1	E2		E4	E5	E6
	50 000	44000	43700		39500	34700	37000

where F_a and F_l represent the weight of the sample in air and in liquid (deionized water with the density ρ_l).

The results of some selected samples with steadily increasing $\bar{M}_v$ are summarized in Table II. Thermal characteristics, such as melting temperature T_m, heat of fusion ΔH, thermal expansion coefficient α, could be determined by the use of Differential Scanning Calorimetry (DSC) both of the system TA 4000 of Mettler and a Thermal Mechanical Analysis (TMA) facility. The scanning rate for DSC measurements was 10 K/min, the range was 30–300°C, sample weight amounted between 6–7 mg, and measurements were carried out in air. Temperature callibration was performed by means of indium, lead and zinc.

The degree of the crystallinity X_c was calculated from the DSC plots using the common equation:

$$X_c = \frac{\Delta H}{\Delta H^0} \cdot 100\% \tag{2}$$

where ΔH is the measured heat of fusion, and $\Delta H^0 = 240\,\mathrm{J/g}$ is the heat of fusion of the fully crystalline PA 6 [6].

TMA measurements were performed on selected samples to demonstrate the effect of molecular weight and annealing temperature T_a on the thermal expansion coefficient; for these experiments a heating rate of 2 K/min, a sample thickness of 3.5–4.5 mm and a load of 0.05 N was applied. The DSC and TMA results are presented in Table II.

The humidity in PA 6 was determined according to the German Standard DIN 53495 requirements. The samples have been dried for 24 h at 80°C. It is known that this kind of treatment does not completely remove the absorbed water (mostly because of hydrogen bonding). But in the present case the purpose of these measurements was to compare the amount of water removed during this standard method of drying, for samples differing in their molecular weight and thermal pretreatment. The results are summarized in Table II.

Similar to all other polyamides, PA 6 exhibits a polymorphism. The basic crystalline modifications are the monocline α-structure, stable at higher temperatures, and the monocline γ-structure, which is present only at lower temperatures (up to 150°C). As the two modifications differ in their crystalline density, it was of interest to known which on existed in the various samples after thermal treatment. For this reason

TABLE II Density ρ, melting temperature T_m, heat of fusion ΔH, crystallinity X_c, thermal expansion coefficient α, humidity content after thermal treatment Δh, predominating α- or γ-crystalline modification (mod.), shear melt viscosity η of PA 6 samples differing in their molecular weight and thermal treatment

Sample	$\bar{M}_v$ [g/mol]	ρ [g/cm^3]	T_m [°C]	ΔH [J/g]	X_c [%]	α		Δh [%]	*mod.*	η [Pas]	$\dot{W}_s$ [$10^{-6} mm^3/Nm$]
						$< T_g$ [$10^6/K$]	$> T_g$ [$10^6/K$]				
A1	9600	1.1418	220.5	72.1	30.04	171.3	234.6	1.07			5.34
2	9400	1.1480	220.6	76.9	32.04			1.06			4.80
4	8700	1.1487	220.4	75.6	31.50			1.03		34.72	5.98
5	7600	1.1574	221.7	77.8	32.41			0.88			5.73
6	8400	1.1670	227.3	89.0	37.08	99.2	122.0	0.86			3.15
B1	17800	1.1432	220.5	71.4	29.75	87.6	149.4	1.04	γ	308.4	4.27
2	17600	1.1455	222.8	77.8	32.42			1.05			4.23
4	17200	1.1526	221.6	70.7	29.46			0.99			3.04
5	14800	1.1634	221.7	77.2	32.17			0.89	α		3.14
6	17000	1.1683	224.5	84.6	35.25	118.2	152.7	0.83	α		3.51
C1	27000	1.1345	222.8	73.9	30.79	111.2	148.2	1.18		3024	4.06
2	28500	1.1385	221.7	67.5	28.13			1.06			2.68
3	28600	1.1394	222.8	76.7	31.96			1.02			2.19
5	35500	1.1484	224.1	68.3	28.46			0.94		3437	2.24
6	51000	1.1545	222.4	81.9	34.13	119.7	148.1	0.85		7185	2.92
D1	33600	1.1347	221.8	68.3	28.46	127.7	110.4	1.00	γ		3.35
2	33800	1.1363	221.8	68.7	28.63			1.09			3.09
4	34700	1.1388	222.8	72.7	30.29			1.05			2.08
5	41400	1.1457	221.8	80.2	33.42			0.95	α		3.18
6	47400	1.1591	224.8	79.6	33.17	127.6	142.8	0.86	α		4.42
E1	44000	1.1387	224.1	67.6	28.17	154.3	183.9	1.21			2.32
2	43700	1.1360	220.5	74.9	31.21			1.01			2.23
4	39500	1.1390	224.0	66.2	27.58			1.02			2.69
5	34700	1.1506	221.6	70.8	29.50			0.96			2.88
6	37000	1.1575	221.5	75.5	31.46	122.4	132.4	0.92		4904	2.53

IR-measurements (with an IR-microscope Nic Plan of Nicolet) were carried out using three samples of two different groups that strongly differed in their thermal treatment. To achieve a high transmission rate, thin slides were prepared and placed on KBr-plates. All measurements were carried out in a wave number range between 4000 and 400 cm^{-1}. The different absorption bonds of α- and γ-modification as a result of transmission measurements allow to distinguish between the two. The presence of either α- or γ-modification can just be proved by analysing the IR-spectrum. Assignment of the IR-bands to the respective α- or γ-modification was made according to the results of Illers and Haberkorn [7].

Table II presents the predominating modifications observed in the samples selected.

The most characteristic feature to describe the differences between the samples is the melt viscosity η. The determination of η was carried out in a Mettler-Suck rotation rheometer of type V10, a plate-plate-rheometer of Couette-type. During measurement a shear rate $\dot{\gamma}$ is set and the resulting shear stress τ is measured. The corresponding shear viscosity $\eta(\dot{\gamma})$ is calculated according to:

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{3}$$

The measurements were performed in air under the following conditions: diameter of the plate 20 mm, distance between the plates about 4 mm, maximum shear rate of 0.1 s^{-1}, measuring time of 1 min, holding time of 0.1 min, and measuring temperature of 250°C. The results are listed in Table II as well.

2.3. Tribological Measurements

Sliding wear experiments were performed with a "block-on-ring" test configuration close to ASTM G 77. The specimens had dimensions of $4 \times 4 \times 6\,\mathrm{mm}^3$ and were machined out of the center part of the "dog-bone" samples. Tests were carried out under the following conditions: room temperature environment, as counterpart a rotating ball bearing cylinder, 60 mm in outer diameter, made of German Standard 100Cr6 steel, surface roughness of 0.1 – 0.2 μm, apparent contact surface area of 16 mm^2, normal force of 16 N, apparent contact surface pressure of 1 N/mm^2, rotation velocity of 1 m/s, run-in time of 15 h, and a subsequent test duration of 6 h. Prior to testing, the steel rings were cleaned in acetone. A fresh surface was used for each test. Four specimens from the same sample were tested simultaneously. The weight of each specimen was checked 24 h after completing the wear experiment. Because the experiments were not carried out in a special chamber under N_2, the effect of humidity absorption during testing was calculated by weighing a reference sample not subjected to wear testing.

The worn volume ΔV is frequently referred to the sliding distance L and the apparent contact surface A_0 as follows:

$$\dot{W} = \frac{\Delta V}{L \cdot A_0} \tag{4}$$

If the dimensionless wear rate $\dot{W}$ is divided by the apparent contact pressure p, it transfers into the specific wear rate $\dot{W}_s$. The latter can also be expressed through the weight loss Δm, which is related to the sliding distance, the material's density ρ and the applied normal force F_N, according to:

$$\dot{W}_s = \frac{\Delta m}{L \cdot \rho \cdot F_N} \tag{5}$$

where $p = F_N/A_0$ and $\Delta V = \Delta m/\rho$.

The specific wear rate $\dot{W}_s$ (Eq. (5)) has the dimension of volume/energy and describes how much energy is needed to remove a certain volume of material. Therefore $\dot{W}_s$ is probably the most proper characteristic for considerations on the influence of material properties on its wear behaviour. However, one should not forget, that wear is not really a material property, but a property of the system in which two materials have to function in relative contact motion to each other [8].

3. RESULTS AND DISCUSSION

3.1. Morphological Characterization After Various Treatments

Because the wear behaviour of polymeric materials strongly depends on their chemical composition and their morphological structure, it is important to have as much information as possible *e.g.*, about their degree of crystallinity, their crystal perfection, melting temperature, glass transition temperature, *etc.*, before wear tests are carried out. The most common way to determine the degree of crystallinity X_c is by density measurements, for which however knowledge about the density of the completely crystalline polymer is necessary. In the present case the density technique didn't seem to be the most proper way, because the presence of polymorphic modifications in polyamides requires further information about the amount of each modifications in a given sample. For this reason the heat of fusion ΔH, determined by DSC, was used for evaluation of the degree of crystallinity. The results are given in Table II. Surprisingly, the expected differences in X_c values for samples differing in molecular weight and thermal treatment could not be observed. The variations obtained were within the standard deviation interval. A possible reason for the almost equal degree of crystallinity is the well known recrystallization phenomenon. It has been demonstrated [3], that polyamides that are thermally treated at low temperatures, undergo a recrystallization during scanning in the calorimeter. The registered melting enthalpy ΔH and the melting temperature result from crystals, that appear during scanning, but not from crystals, created during the original thermal treatment [9]. This assumption is confirmed here by the values of T_m, which are almost the same for all samples. Additional support for this statement can be found in the shape of the thermograms; samples annealed at low temperatures showed a double peak in some cases, which is related to recrystallization during measurement, as demonstrated by Illers *et al.* [10]. The melting peaks show a different pecularity, related to their shape. Although the areas of the peaks are almost the same; they differ substantially with respect to their form. Samples annealed at higher temperatures (220°C) show extremely sharp and up to two or three times sharper melting peaks in comparison to samples which were annealed at lower temperatures. To conclude this point, it can be stated, that the DSC technique did not provide good information about the crystallinity of the samples differing in their molecular weight and thermal treatment conditions. For this reason it was decided to use the density data, for demonstrating the effects of thermal treatment, but not as characteristic values for the evaluation of crystallinity. In Figure 1 the effect of the annealing temperature T_a on the density is plotted for samples with

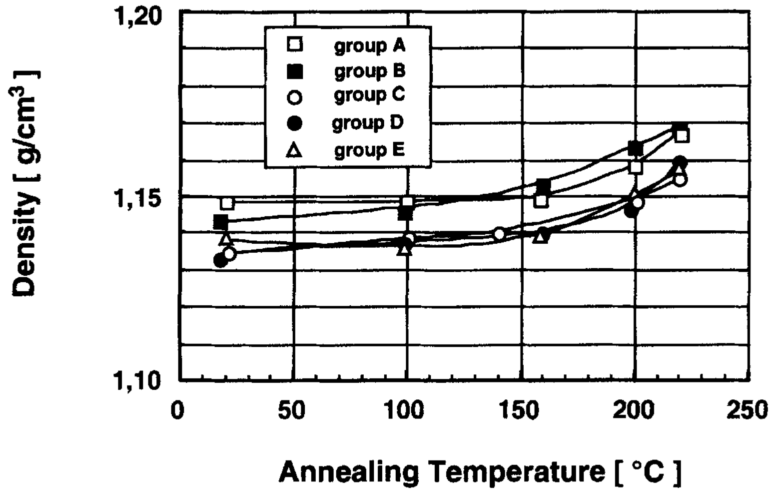

FIGURE 1 Effect of annealing temperature on density of various types of PA 6 samples (for samples designation see Tab. I).

various molecular weights. One can see that the density increases with the rise of T_a. In addition, as one can expect, that samples with the lowest molecular weight have the highest density, whereas those with higher molecular weights show the lowest density values.

This last dependency is expressed in Figure 2, in which the density of samples treated at different annealing temperatures are plotted as a function of their molecular weight. Density decreases with rising molecular weight, not depending on the thermal pretreatment.

An attempt was made to evaluate the dominating crystalline modification after thermal treatment with IR-microscopy. The measurements carried out with unannealed (B1 and D1) and at 200°C or 220°C annealed samples (B5 and B6; D5 and D6, Tab. I) show that the last two types of samples contain only α-modification, whereas in the first one both, γ- and α-modification are present (Tab. II). The results described were derived from measurements performed on two sample groups (B and D) with molecular weights of about 20 000 and 40 000 respectively, but they should also be valid for samples with other molecular weights.

Of particular importance for the wear experiments is also the thermal expansion coefficient α, because it may increase during wear

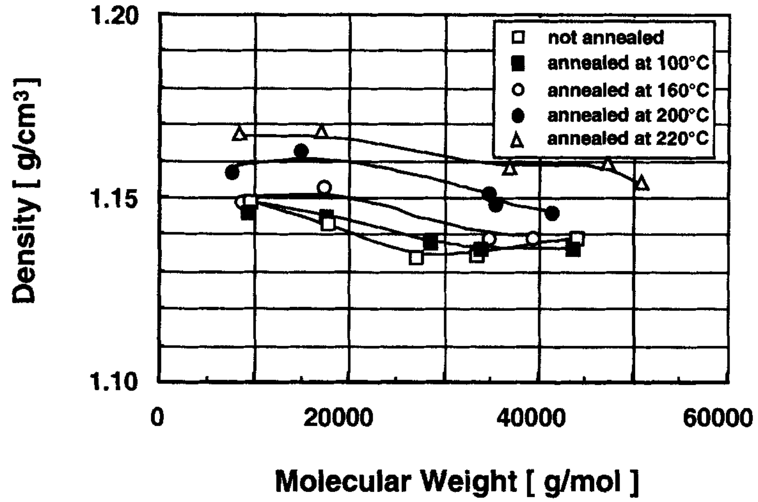

FIGURE 2 Effect of molecular weight on density for PA 6 samples, annealed at various temperatures.

testing as a result of an increase in specimen temperature; this may lead to an enhancement in the material's wear rate. Therefore the thermal expansion coefficients of samples with very strongly varying pretreatment conditions were also determined (Tab. II). A plot of these values *vs.* the molecular weight of the samples (Fig. 3) illustrates, that two values for α were obtained, one characteristic for the temperature range below the glass transition temperature T_g of the various materials, and the other for temperatures above it. The most striking observation was, that the thermal expansion coefficients for temperatures below and above T_g did hot significantly depend on the molecular weight in case of samples that were annealed at higher temperature (220°C) (samples of series 6, Tab. I). This means, that such a treatment results in a rather stable morphological structure which should not remarkably change, if a wear test is applied. This was not the case for samples without annealing (samples of series 1, Tab. I). One can also see from Figure 3, that α changes in an irregular way with an increase in molecular weight or annealing temperature. Samples with an unstable structure like this can more easily undergo a recrystallization process during wear, that may affect their wear characteristics more drastically.

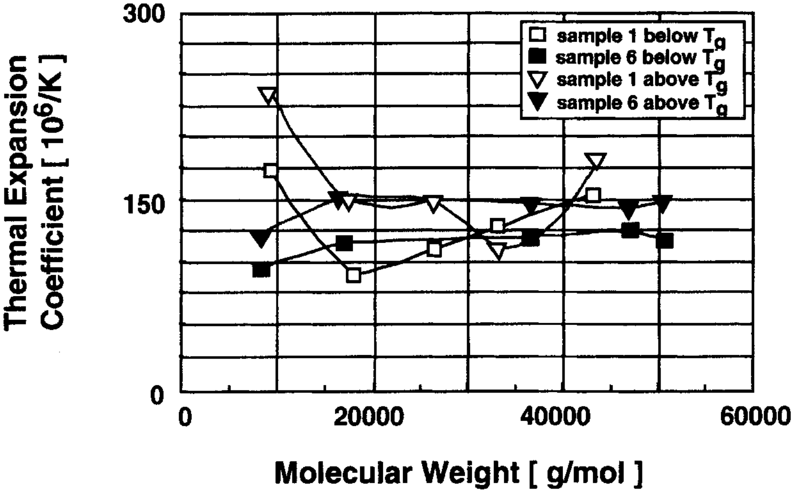

FIGURE 3 Thermal expansion coefficient in function of molecular weight of various PA 6 samples (for samples designation see Tab. I).

The last characterisation measurements were related to the humidity situation of samples differing in their molecular weight and thermal treatment. The drying was performed in a way typical for commercial conditions. The purpose of this measurement was not to obtain completely dried material, as mentioned above, but to evaluate the amount of water removed after treatment. The results (Tab. II) show, that all the samples under investigation lose the same amount of water after drying for 24 h. The scatter between them was only about 1%. It must be considered, however, that after the drying procedure still a relatively large amount of water remained in the samples. This water acts for polyamides as a good plasticizer which strongly decreases the glass transition temperature, and thus should also affect the wear behaviour.

3.2. Wear Behavior

Figure 4 illustrates the dependence of the specific wear rate $\dot{W}_s$ on the annealing temperature T_a for samples differing in their molecular weight. In general it can be stated, that $\dot{W}_s$ is only slightly influenced by the annealing temperature, particularly for samples with the highest

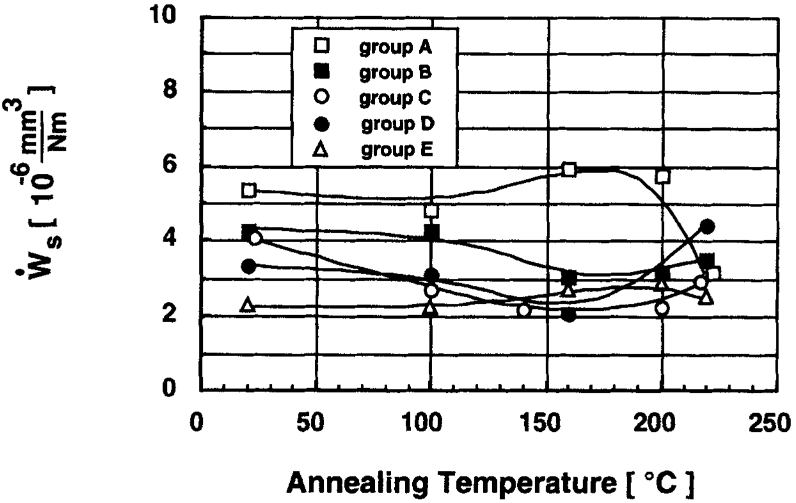

FIGURE 4 Specific wear rate in function of annealing temperature for PA 6 samples with various molecular weight (for samples designation see Tab. I).

molecular weight. The latter exhibited, in addition, lower wear rates than those with the lowest molecular weight. However, annealing of the samples with lower molecular weights at a sufficiently high temperature (220°C) dropped also their wear rates down to the lower level, as measured for the samples with higher molecular weights. The reason for this relatively strong change in the specific wear rate is related to the most stable physical structure which is obtained after annealing at this temperature. This statement is supported by density measurements (Tab. II, Fig. 1) from which one can conclude that just the two samples with the lowest molecular weight after annealing at 220°C show the highest density.

The effect of the molecular weight on the specific wear rate $\dot{W}_s$ is displayed more clearly in Figure 5. First of all one can see, that the specific wear rate does not depend on the molecular weight, if the samples have been annealed at the highest temperature (lower bound of the scatter range). For the rest of the samples one can see a well expressed tendency for a decrease of the $\dot{W}_s$ values with a rise of molecular weight (upper bound of the scatter range). While the effect of the annealing temperature on the specific wear rate (Fig. 4) is mostly related to changes in the crystalline morphology of the samples (making

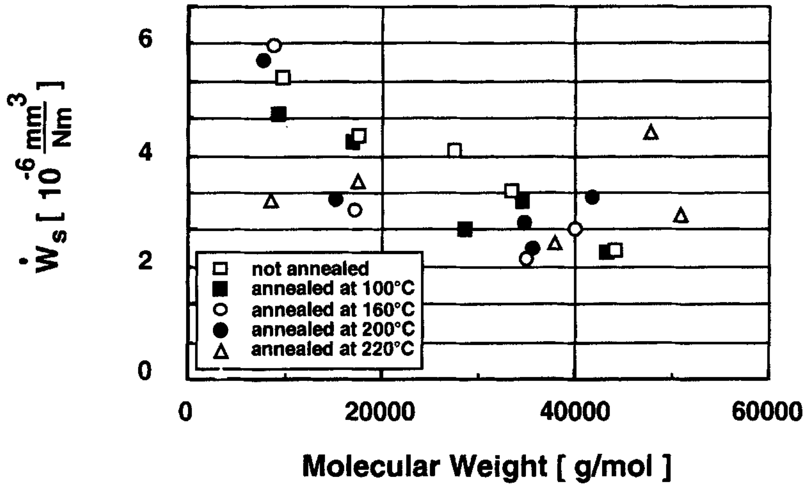

FIGURE 5 Specific wear rate for PA 6 samples annealed at various temperatures in function of molecular weight.

their surfaces harder with an increase in X_c), the effect of the higher molecular weight (Fig. 5) should be primary connected to the stronger entanglement of the polymer molecules. The latter leads to a higher toughness of the bulk, and it should also be expressed in a higher shear viscosity of the surface. For this reason measurements of the shear viscosity of samples differing in their molecular weight were carried out. The results, summarized in Table II and plotted in Figure 6 (η as a function of the molecular weight), illustrate that the viscosity strongly depends on molecular weight. While samples with the lowest molecular weight (around 10 000) have η values of only 35 Pas, those with a molecular weight of about 50 000 have a shear viscosity of up to 7 200 Pas. Only by such a drastic change in the melt viscosity (Fig. 6) one can explain the strong drop (2–4 times) of the specific wear rate with a rise of molecular weight (Fig. 5). The strong effect of the shear viscosity of the samples on the specific wear rate can be seen in Figure 7.

Three characteristic zones of the specific wear rate W_s can be distinguished. The first one is characterized by the highest value of $\dot{W}_s$, corresponding to the sample with the lowest viscosity η of 35 Pas, which is typical for PA 6 with a molecular weight around 10 000. The second zone is the medium one with respect of the values of the $\dot{W}_s$ and

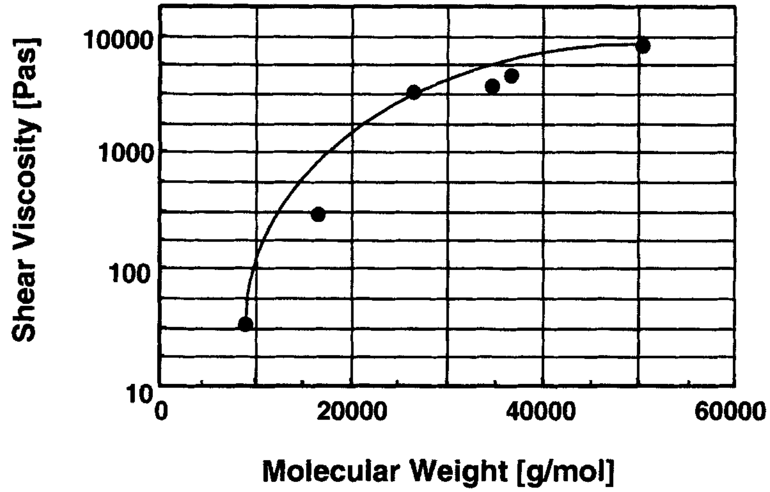

FIGURE 6 Effect of molecular weight on shear viscosity for PA 6 samples.

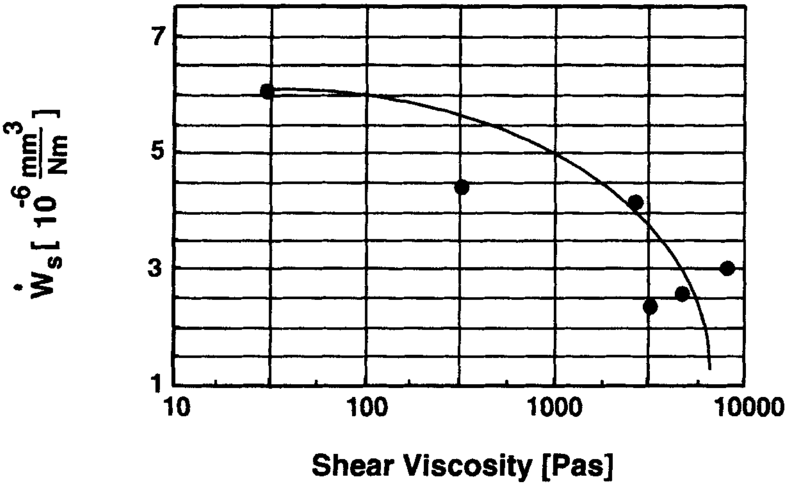

FIGURE 7 Relationship between specific wear rate and shear melt viscosity of PA 6 samples.

corresponds to the samples with a viscosity between 300 and 3 000 Pas (molecular weights between 20 000 and 30 000). The third zone covers the samples with the lowest specific wear rate. These samples have the highest viscosities (3 000 – 7 000 Pas) which are characterized also by the highest molecular weights (30 000 – 50 000). Actually the curve shown in Figure 7 demonstrates in the best way the dominating role of the polymer viscosity on its wear behavior.

4. CONCLUSIONS

To determine the wear behavior of PA 6 samples, varying in their molecular weight and thermal treatment, not only tribological measurements were carried out since it is important to have an idea about the physical structure of the material. The density increases with increasing annealing temperature but it decreases with the rise of molecular weight. The thermal expansion coefficient was measured as a function of molecular weight of unannealed samples and samples annealed at 220°C. For both cases below and above T_g the thermal expansion coefficient does not depend on the molecular weight when the samples are annealed at the highest temperature (220°C). This proves that annealing at high temperatures results in a rather stable physical structures. In contrast, not annealed samples do not show a linear relationship between the thermal expansion coefficient α and molecular weight. These results are important for the wear behavior of the material. Obviously, a stable physical structure will not change during the wearing process whereas samples with an unstable structure (unannealed samples) can recrystallize during wearing. The shear viscosity can range from 35 Pas to 7200 Pas when the molecular weight ranges from 10000 to 50000.

The wear behavior of the samples with the lowest molecular weight is very sensitive to the annealing temperature; after annealing at high temperatures they reach a $\dot{W}_s$ value which is typical for samples with high molecular weight. For intensively annealed samples the specific wear rate does not depend on the molecular weight. For the rest of the samples there is a clear tendency for a decrease of $\dot{W}_s$ values with a rise of molecular weight.

So the wear behavior of this materials is influenced by two different factors. On the one hand, there is a tendency for a decrease of $\dot{W}_s$ values with increasing annealing temperatures, especially for samples with low molecular weights because of the formation of a more stable physical structure. On the other hand, there is a well defined tendency for a decrease of $\dot{W}_s$ values with a rise of molecular weight, except for the intensively annealed samples which do not show any dependence from molecular weight. This strong effect of molecular weight is related to the observed drastic increase of viscosity with an increase of molecular weight.

Acknowledgements

The financial support of the Deutsche Forschungsgemeinschaft (DFG FR 675/21 – 1) and of the Bulgarian Ministry of Education and Science (Grant Nr. X-542) is gratefully acknowledged. Prof. K. Friedrich expresses his thanks to the Fonds der Chemischen Industrie, Frankfurt, for support of his personal research activities in 1999.

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