

Methods for Predicting the Quality of Nylon 612 Filament for Use as a Bristle Material

H. RALPH RAWLS,^{1,*} ROBERT CASELLA,¹ VERNE BACKUS,² and ROBERT DILL²

¹Department of Dental Research, The Gillette Company, 1 Gillette Park, Boston, Massachusetts 02106;

²E. B. & A. C. Whiting Company, Burlington, Vermont 05402

SYNOPSIS

Splaying and curling of bristles is a very important performance characteristic of nylon toothbrushes. For this reason, analytical methods are needed that correlate fundamental physical-chemical properties with the eventual development of bristle splaying. Differential scanning calorimetry, thermogravimetric analysis, and wide-angle X-ray diffraction were each found to identify subtle differences in nylon 612 filament that had been subjected to varying processing conditions during manufacture. These differences were found to be related to water absorption and crystalline perfection and could be correlated with the characteristics of toothbrush wear. From the results, it was concluded that these three methods can be used for quality control and research purposes to predict and to study end-use performance factors such as bristle splaying. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Most toothbrushes are made from nylon 612 filament. With use, the nylon bristles take on a permanent curl along the outer one-third of their length. This "splaying" process eventually leads to reduced cleaning efficiency and to the perception that the brush is "worn out." Filament recovery from bending and machine "scrub" tests are currently used to predict this performance. Such tests are time-consuming, are highly subject to experimental variability, and give only minimal insight into fundamental properties. Thus, analytical methods are needed that rapidly provide information about fundamental physical-chemical properties that are predictive of end-use performance.

Wearing out through the development of bristle splaying is one of the most important performance properties of brushes. As part of an effort to ensure consistent filament quality, nylon 612 filament was investigated using thermal analysis and X-ray diffraction techniques. The filament samples were

taken from both commercial and experimental batches. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and wide-angle X-ray diffraction (WAXD) were found to be useful for identifying subtle differences among filaments from the various sources. These differences could be correlated to the process conditions used in making the filaments and were found to be predictive of the development of bristle splaying in toothbrushes.

EXPERIMENTAL

Materials

The various filaments and the brushes made from them are described in Table I. Samples of nylon 612 filament were taken from both experimental and production lots. The experimental filament was extruded from molten ZYTEL 158TM (E. I. duPont) on an industrial spinning line in which the normal thermal processing conditions (quenching, primary and secondary annealing) were varied so as to produce a range of densities and "bend recovery" values as shown in Table I. Bend-recovery is a quality-assurance test method that measures the recovery of filament wound around a 2.4 mm (3/32 in.) mandrel and held in place for a specified time at a constant

* To whom correspondence should be addressed at The University of Texas Health Science Center, Division of Biomaterials, San Antonio, TX 78284-7890.

Table I Filament Materials and Types of Brushes Sampled

Filament Sample	Processing Conditions ^a	Density ^b (g/cm ³)	Bend-recovery	Type of Brush ^c
<u>Experimental Filament</u>				
E1/83	1° anneal lowered by 150°C 2° anneal eliminated	1.0587	83.0	Adult
E2/90	Quench raised by 52°C 2° anneal eliminated	1.0683	90.5	Adult
E3/92	2° anneal eliminated	1.0675	92.5	Adult
E4/97	No change from normal manufacturing process	1.0709	96.7	Adult
E5/98	2° anneal lowered by 24°C	1.0648	98.0	Adult
<u>Production Filament</u>				
CB/78	Unknown	< 1.0620	~ 78 ^d	Child
CB/96	Unknown	1.0680	~ 96 ^d	Child
CH/97	Unknown	1.0676	96.7	Hank ^e

^a Changes from normal, proprietary, manufacturing process conditions.

^b Measured using a density-gradient column.

^c Adult-size brushes were ORAL-B P40[®]; child-size brushes were MUPPET[™] (Oral-B Labs).

^d Samples retrieved from brushes were too small for the mandrel bend-recovery measurement. Values were estimated by looping filaments inside a hole 11 times their diameter, holding for 4 min, and measuring the percentage angular recovery after 1 h in ambient air.

^e Strands were taken from a production-lot hank of filament, not from a brush.

humidity.¹ This filament was used to form the bristles in adult-size toothbrushes (ORAL-B P40,™ Oral-B Laboratories, Inc.) using high-speed production equipment. Three additional filament materials were taken from nonexperimental, routine production sources. Two were retrieved from children's size toothbrushes (MUPPET™, Oral-B Labs.). One of these, CB/78, had been withdrawn from distribution as a result of consumer complaints that the brushes wore out too quickly (i.e., premature splaying). The other, CB/96, was taken from a toothbrush lot that had received no consumer complaints. The third commercial filament, CH/97, was sampled from a "hank" of production nylon filament from a different batch of the same manufacturer as sample CB/96 (TYNEX™ filament, E. I. duPont). This sample was not used to prepare toothbrushes.

Brush Wear

Two methods were used to produce toothbrush wear: human-usage and a scrub-test brushing machine. The brushing machine produces a lifelike pattern of toothbrush splaying.² Splaying denotes the type of toothbrush wear that results when bristles spread apart and curl during use. Splaying was determined by measuring the *wear index*, as described by Rawls et al.,³ before and after use. Laboratory wear-tests were performed by mechanically scrubbing brushes against porcelain denture teeth covered by a tooth-

paste slurry. The teeth were moved 7000 revolutions in a figure-eight pattern while the brush heads were held under a static load of 700 g. We described this method earlier² and showed that an excellent correlation exists with the splaying produced during 16 weeks of average human use.²

Two of the production filaments, CB/78 and CB/96, were only available as bristles in already-made toothbrushes. We had only six toothbrushes with each of these two filaments, which necessitated a very small human-use test. For this reason, one person was chosen who had served in a larger panel study and was known to produce a very consistent pattern of splaying at about six times the rate of the average individual. Each brush was used by this individual for a full week at home without supervision, alternating between brushes made from CB/78 and CB/96.

Thermal Analysis

A DuPont thermal analyzer 1090B/1091 equipped with a 951 TGA and DSC cell base was used to measure the thermal properties of nylon filaments. Analysis variables were as follows:

1. DSC samples were heated at 5°C/min from 25 to 130°C, and at 20°C/min from 130 to 300°C.

2. N_2 was passed through the DSC cell at 50 ± 10 mL/min and through the TGA cell at 100 ± 20 mL/min.
3. Transition enthalpies were calculated by integrating the water vaporization endothermal transition from 30° to 125°C and the crystalline melting endotherm from 160° to 280°C .
4. DSC and TGA samples were equilibrated 48 h at 100% relative humidity.
5. TGA samples were heated at $5^\circ\text{C}/\text{min}$.
6. TGA water loss was calculated from the weight change that occurred between 25 and 125°C .

Wide-angle X-ray Diffraction (WAXD)

An X-ray diffractometer (Siemens A. G., Germany) with the following instrumental parameters was used to determine wide-angle diffraction patterns:

1. Nickel-filtered copper, K-alpha radiation was used at 30 kV and 28 mA.
2. The divergence and receiving slits were set at 1 and 0.4° , respectively.
3. The time constant was 10 s, and the intensity (counts/s) was 4×10^2 .
4. The scanning rate and chart speed were $2^\circ/\text{min}$ and 1 cm/min, respectively.
5. The scan range was $6\text{--}40^\circ$ of the diffraction angle, 2θ .
6. Samples were equilibrated for at least 48 h at 50% relative humidity (RH) and prepared for analysis by cutting 3.8 cm lengths from ~ 70 different 0.02 mm nylon filaments (all taken from the same manufacturing or experimental batch) and mounting these lengthwise on a glass plate with petroleum jelly.

Neither the petroleum jelly nor the glass produced a diffraction peak in the scan range, but a slight amorphous scattering halo did appear. The angular separation of the two diffraction peaks was used to measure crystalline perfection, expressed as Δd .⁴ These peaks represent the (100) and (010), (110) crystalline reflections of triclinic nylon as influenced by superimposed scattering from amorphous nylon.⁴

RESULTS

Specimen Conditioning (Moisture Content)

Initially, specimens used for thermal analyses and WAXD were equilibrated for 48 h at 0, 50, and 100%

relative humidity (RH). However, it was found that differences in water absorption could be observed in DSC and TGA only when conditioning was at 100% RH (at room temperature, $\sim 23^\circ\text{C}$). The WAXD spectra were observed to change slightly with humidity, but these changes were proportionate in all samples. Thus, the relative crystallinities remained constant for constant equilibration humidity. Ambient conditions were usually close to 50% RH and the scans often required several hours. Therefore, to prevent the water content from changing significantly during the course of a measurement, 50% RH was used to equilibrate the WAXD specimens.

Wear Testing

The development of machine-induced wear by brushes made from the experimental filament materials is shown in Figure 1. No significant differences in wear index were observed except for E1/83. This sample had the lower bend recovery value (Table I) and produced the higher wear index ($P < 0.01$).

As shown in Table II, the premature wear reported for filament CB/78 was confirmed in a human brushing trial at the Gillette Dental Research Laboratory. CB/78 had almost twice the wear index of the control filament, CB/96. CB/96, which was taken from a production lot for which there were no consumer complaints, developed splaying at a rate known from separate experiments to be normal for the subject who used these brushes.

Thermal Analyses (DSC and TGA)

Typical DSC thermograms are shown in Figures 2 and 3. The DSC results revealed two interesting re-

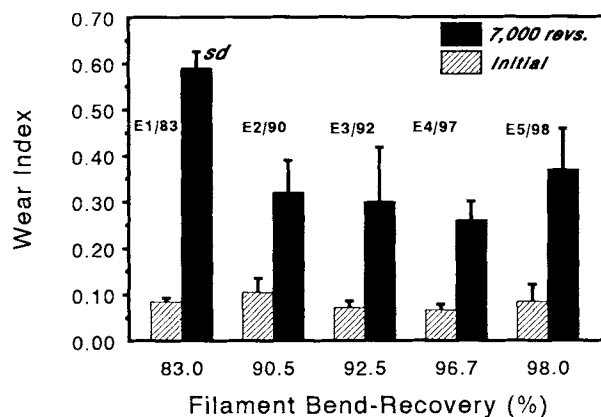


Figure 1 Wear index values of ORAL-B P40 toothbrushes containing experimental nylon 612 filament that had been processed as described in Table I.

Table II *In Vivo* Wear Durability of Brushes Made from Production Filaments

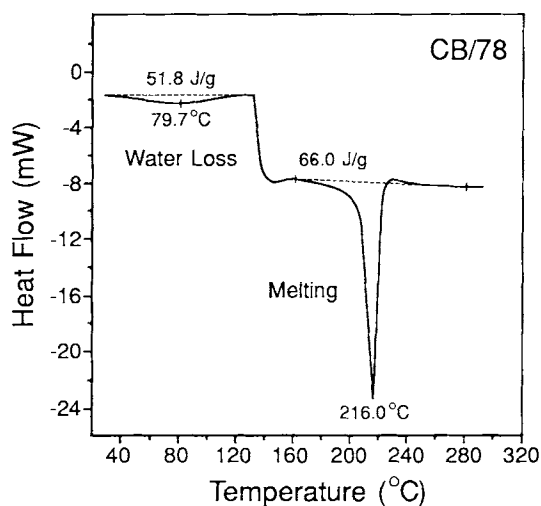
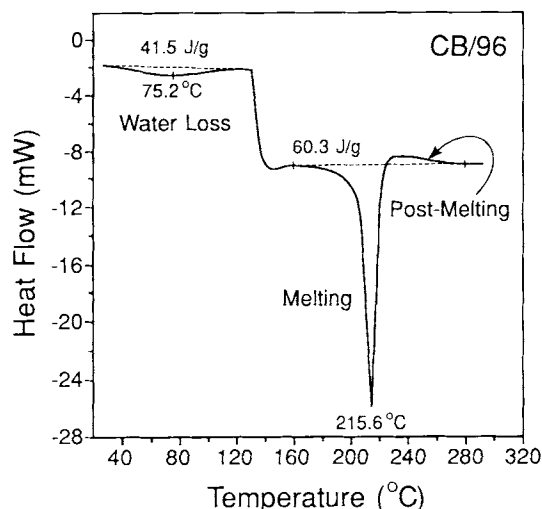
Filament	Brushing Time (Days)	Wear Index ^a
CB/78	0	0.114 ± 0.023
CB/78	7	0.562 ± 0.168 ^b
CB/96	0	0.081 ± 0.003
CB/96	7	0.317 ± 0.066 ^b

^a Average of two brushes ± SD.

^b Values that are different from each other at $P < 0.05$ according to Student's *t*-test.

gions that we found to be related to toothbrush durability. The first, a low-temperature transition between 30 and 125°C, was confirmed by TGA (using both desiccated and hydrated filament specimens) to be a result of water loss—almost certainly from the amorphous phases.^{5,6} The other, from 160 to 280°C, was confirmed by WAXD to involve crystalline and amorphous phase melting, reorganization, and recrystallization. These processes depend upon the thermal histories of the filaments during manufacture and storage.^{4,6}

DSC showed that the two low-density, low-bend recovery materials, E1/83 and CB/78, are similar to each other and significantly different from the other filament materials in two ways. E1/83 and CB/78 have a larger endothermal transition in the water-loss region and lack a significant postmelting exotherm near 230°C. These features are illustrated in Figures 2 and 3 and in Table III. TGA showed that the two low-bend recovery filaments also absorb

**Figure 2** DSC thermogram of production filament with bend-recovery $\approx 78\%$.**Figure 3** DSC thermogram of production filament with bend-recovery $\approx 96\%$.

more water, as illustrated in Table III with CB/78. When heated, filament CB/96 loses only 2.0% water, while CB/78 loses 2.6%. This increased capacity for water absorption is most likely a result of either a larger amorphous phase or greater disorder in the amorphous/semicrystalline structure, or both. This is discussed further below.

A close examination of Figure 3 reveals that filament CB/96 has a distinct postmelting exotherm near 230°C. CH/97 also has this exotherm, but it is absent in the low-bend-recovery filament, CB/78, as shown in Figure 2. The melting endotherms of CB/96 and CB/78 show no quantitative difference (Table III). However, we found that *qualitatively* the small postmelting exotherm was present

Table III Water-Loss and Melting Enthalpies in Nylon 612 Production and Experimental Filament Equilibrated at 100% RH

Filament	Water Loss (25–125°C)		Melting ($\sim 216^\circ\text{C}$)
	TGA (% w/w) ^a	DSC (J/g) ^{a,b}	DSC (J/g) ^a
E1/83	—	47.9 ± 10*	77.3 ± 5.2
E2/90	—	47.5 ± 2.5*	81.0 ± 7.0
E3/93	—	40.2 ± 4.2**	76.0 ± 1.2
E4/97	1.9	39.1 ± 1.6**	74.5 ± 1.0
E5/98	—	39.2 ± 4.1**	77.6 ± 4.2
CB/78	2.6	49.4 ± 2.4*	63.8 ± 7.3
CB/96	2.0	39.4 ± 1.9**	60.7 ± 2.2

^a Average of three measurements ± SD.

^b Values with equal number of asterisks, * or **, are not significantly different at $P < 0.05$ according to Student's *t*-test.

in all of the filaments studied that had bend-recovery $\geq 90\%$ and was missing only in E1/83 and CB/78. These also were the same filaments that produced a high rate of splaying when used as toothbrushes (Fig. 1 and Table II).

Richardson⁷ investigated the complex shape of the DSC melting curve of nylon 612 and concluded that the original crystalline form melts at about 200°C but transforms into a second crystalline form at about 220°C. This transformation liberates heat, producing an exotherm, while, at about the same temperature, the second form melts and produces a second endotherm. The resulting curve is a composite of one exothermal and two endothermal transitions. This also has been observed for several other types of nylon^{7,8} and other polymers as well.⁹ The crystalline transformation of nylon is, therefore, a melting/recrystallization/remelting sequence rather than a solid-state, crystal-crystal transformation.⁸ Furthermore, it is considered that the initial melting endotherm originates from relatively small, imperfect crystallites formed during cooling of the spun filament.⁸ Todoki⁵ determined that the two endothermal transitions in nylon 6 result from the reorganization of the crystals formed during filament drawing. These crystals are a mixture of two crystalline orientations that are capable of reorganizing to another higher-melting form during a DSC scan.⁵ Water affects these transformations, and it has been observed that the water content of a filament prior to drawing is especially critical. For example, Todoki⁵ observed that the high-temperature endotherm in nylon 6 decreased as the water content increased. In our work, we observed that in the DSC thermograms the onset and peak temperatures

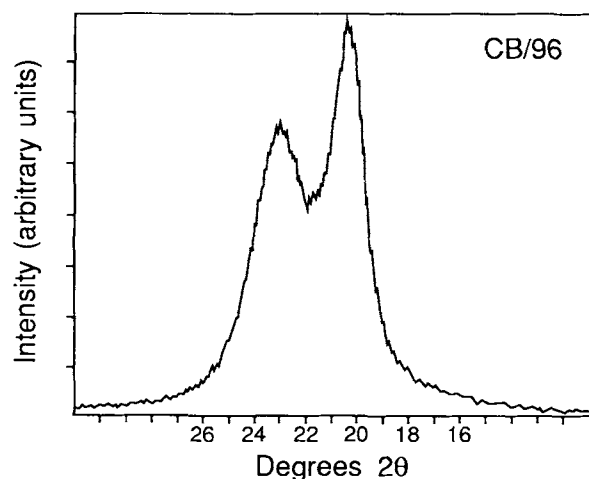


Figure 4 WAXD spectrum of production filament with bend-recovery $\approx 96\%$.

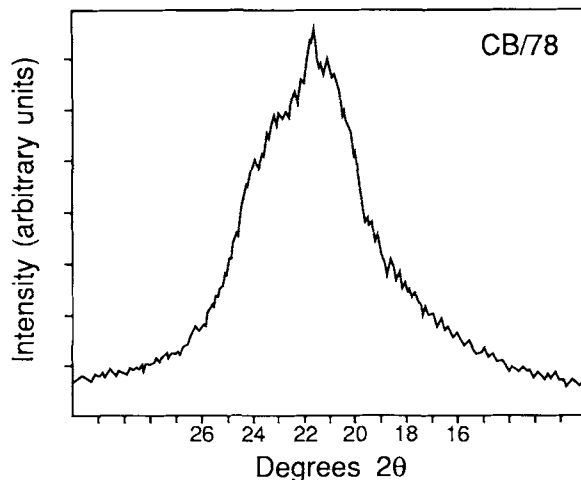


Figure 5 WAXD spectrum of production filament with bend-recovery $\approx 78\%$.

shifted with both the equilibrium moisture content and the thermal scan rate. This behavior is expected for amorphous/semicrystalline/crystalline combination structures such as those discussed above.⁵⁻⁸

WAXD

As with bend-recovery, DSC, and TGA, two types of behaviors are also observed using X-ray diffraction. Typical results with filament having the higher bend-recovery values is shown in Figure 4, in which two well-resolved peaks are seen near 20° and 22° of the diffraction angle, 2θ . The separation between these two peaks, Δd , is a measure of the degree of crystalline perfection. As the degree of crystalline perfection decreases, the diffraction peaks move closer together.⁴ Figure 5 shows the diffraction pattern of the lowest bend-recovery filament, CB/78,

Table IV The Crystalline Perfection of Nylon 612, 0.2 mm Filament as Measured by Diffraction Peak Separation, Δd

Filament	Δd (degrees, 2θ) ^a
E1/83	2.2
E2/90	2.8
E3/92	2.8
E4/97	2.8
E5/98	2.8
CB/78	~ 1.0
CB/96	2.8
CH/97	3.0

^a Measurements taken on a sample containing approximately 70 separate filament specimens.

in which the separation between the peaks is too low to be resolved. This effect is estimated to occur at $\Delta d \leq 1.0$. From this, the crystalline perfection in filament CB/78 is obviously very low (Table IV).

The WAXD analysis for both the experimental and production filaments is shown in Table IV. Comparison of these data with those in Tables I and II and in Figure 1 shows that filaments with a low level of crystalline perfection also display the lower values of density and bend-recovery and the higher wear indexes.

DISCUSSION

The results show that thermal analyses and WAXD can be used to distinguish subtle differences in the amorphous and crystalline phases of nylon filament. These differences are most obvious in the ability of specimens to absorb moisture and in the separation between crystalline diffraction peaks. Nylon 612 filament that has relatively low density and low bend-recovery values also absorbs more water, does not exhibit a postmelting exotherm, and has a relatively low degree of crystalline perfection. This filament also splays more rapidly when used as toothbrush bristles.

Because DuPont nylon 612 (ZYTEL 158™ pellet) was used to produce all the filament materials analyzed here, their differences most likely originate in the filament spinning process. Cooling rate, moisture content and annealing temperatures strongly affect crystallite orientation, the degree of crystal formation, and the degree of chain orientation in the amorphous phase.^{5,6} These observations suggest a connection between the higher equilibrium water uptake and the absence of either a postmelting exotherm or a second endotherm in filament materials that undergo excessive splaying. Various grades of DuPont ZYTEL are sold, and this is another variable that may account for some or all of the differences among the various sources of filament.

CONCLUSIONS

From the above, we may conclude that a permeable, amorphous polymer chain orientation and too little crystalline perfection result in an inferior bristle material. Thermal methods (either DSC or TGA)

or WAXD are good analytical methods for monitoring these subtle factors. Thus, they can be used to predict the durability and ultimate performance of nylon bristle for quality assurance purposes. As alternatives to density, bend-recovery and brush scrub tests, DSC, TGA, and WAXD are readily quantified and less prone to operator/experimental variability. However, they do require expensive instrumentation. WAXD is not sensitive to equilibrium water content and, therefore, does not require extended conditioning. WAXD also produces precise, objective results in a short time. WAXD, therefore, would be the better choice as a quality-control method for monitoring nylon quality. Used together, DSC, TGA, and WAXD are excellent means for studying the effects of process variables and storage and end-use conditions as well as other factors that could affect filament performance via alterations in microstructure.

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