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Microstructure of Cold Fracture Sections as an Indication of Changes in Properties of Injection-Molded Nylon Polymers*

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A considerable literature has developed regarding the crystalline-mesomorphic character and spherulite structure of linear polyamides.[1-7] This lends plausibility to the conjecture that different thermal histories of nylon molded products can lead to different microstructures, and that this causes some of the variability observed in attempting to reproduce consistent physical properties in injection-molded products.

Since greater or lesser degrees of crystalline transition are reflected in density changes, it seemed feasible at first to attempt to correlate physical properties with changes in density, assuming density changes were caused mostly by variations in extent of crystallinity. Density changes in molded items can be induced by heat treatment. Table I shows some average values for several lots of polymers of three types where density changes were induced by annealing at temperatures both far and near from the crystalline melting points.

TABLE I

Nylon type	Crystalline melting point, °C.	Specific gravity				
		A molded	Annealed 17 hr. at 100°C.	150°C.	210°C.	250°C.
66	268	1.14	1.15	1.17	—	1.22
610	228	1.11	1.10	1.12	1.17	—
6	215	1.12	1.12	1.16	1.21	—

Most pronounced differences in density were produced by annealing near the crystalline melting point. Physical properties however, can change markedly after annealing at temperatures considerably short of the region of the melting point. Moreover, the role of water absorption in altering properties or structure complicates the interpretation of density data. In general, either specific gravity measurements at best are not a very sensitive and reproducible index of structure, or else the ratio of crystalline to mesomorphic polymer is not the major factor responsible for altering properties through annealing for the types of nylons commonly used in injection molding. In the attempt to clarify whether or not structural features were important at all in explaining the thermal annealing effects on mechanical properties, a microscopic study was made of three types of injection-molded nylon samples. Because of considerable industrial interest in developing plastics which can be autoclaved, the study was extended to samples which were steamed. The shear modulus and damping properties were measured by the torsion pendulum technique of Nielsen[8] over the temperature range of −40 to 120°C. To minimize oxidative degradation[9] the aging treatments were performed in a relatively oxygen-free environment.

DATA ON DYNAMIC PROPERTIES

Samples were prepared as injection-molded strip from nylons Type 66, hexamethylenediamine adipate (duPont Zytel 101), Type 610, hexamethylenediamine sebacate (duPont Zytel 31), and Type 6, caprolactam polymer (Plaskon 8200). Sample test bar dimensions were 0.125 × 0.250 × 4.950 in.; four samples were treated in each group.

The sample treatments were as follows: (*A*) as molded; (*B*) as molded and annealed for 17 hr. in a vacuum oven at 150°C. or in an oil bath (it seemed to make no difference in the result which was chosen); (*C*) as molded and annealed in a 200° C. mineral oil bath for 17 hr.; and (*D*) as molded and exposed to 120°C. (20 p.s.i.) steam in an autoclave for 24 hr. All samples, after treatment, were stored up to 12 weeks at 23°C. and 50% R.H. before testing. Hence the changes observed here in microstructure and properties are not what

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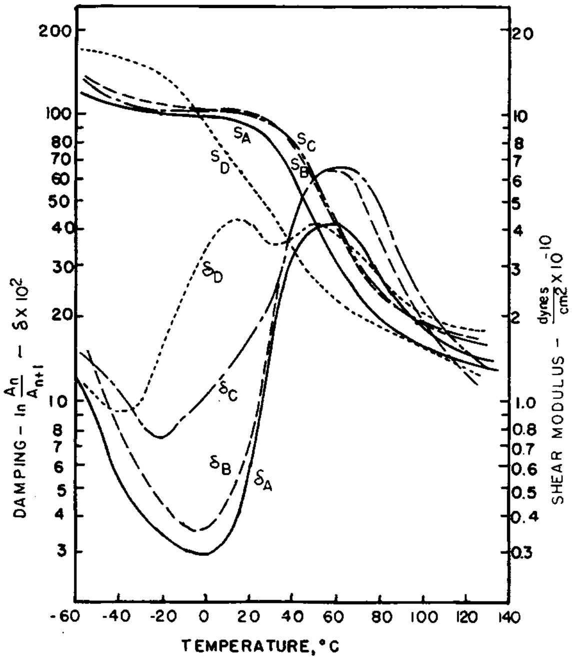

Fig. 1. Shear modulus and damping decrement as a function of temperature for injection-molded nylon 66 (Zytel 101) before and after various thermal treatments and steaming: (——) as molded; (– –) 17 hr. at 150°C.; (— – —) 17 hr. at 200°C.; (- -) 24 hr. at 120°C. steam.

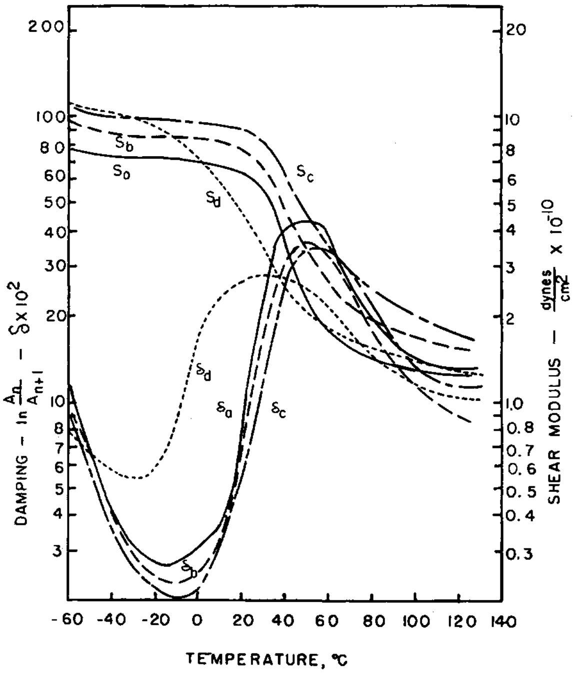

Fig. 2. Shear modulus and damping decrement as a function of temperature for injection-molded nylon 610 (Zytel 31) before and after various thermal treatments and steaming: (——) as molded; (– –) 17 hr. at 150°C.; (— – —) 17 hr. at 200°C.; (—) 24 hr. at 120°C. steam.

TABLE II

Shear Modulus of Annealed and Steamed Nylons at −40, 30, and 100° C.

		Shear modulus, dynes/cm.^{2} × 10^9 at		
		40° C.	30° C.	100° C.
Nylon 66	As molded	10.0	8.00	1.57
	150°C., 17 hr.	11.9	9.50	1.88
	200°C., 17 hr.	11.2	9.23	1.86
	Steam, 24 hr.	15.9	4.65	1.56
Nylon 610	As molded	7.33	5.70	1.33
	150°C., 17 hr.	8.80	6.63	1.70
	200°C., 17 hr.	9.85	8.25	2.00
	Steam, 24 hr.	10.2	3.37	1.40
Nylon 6	As molded	9.80	6.40	1.31
	150°C., 17 hr.	11.9	8.90	1.93
	200°C., 17 hr.	11.8	8.20	1.90
	Steam, 24 hr.	18.0	4.95	2.00

prevail immediately after treatment, but rather are the residual effects such as might persist in storage of molded products. The effects apparent after four weeks of room-temperature conditioning did not change appreciably for several more weeks

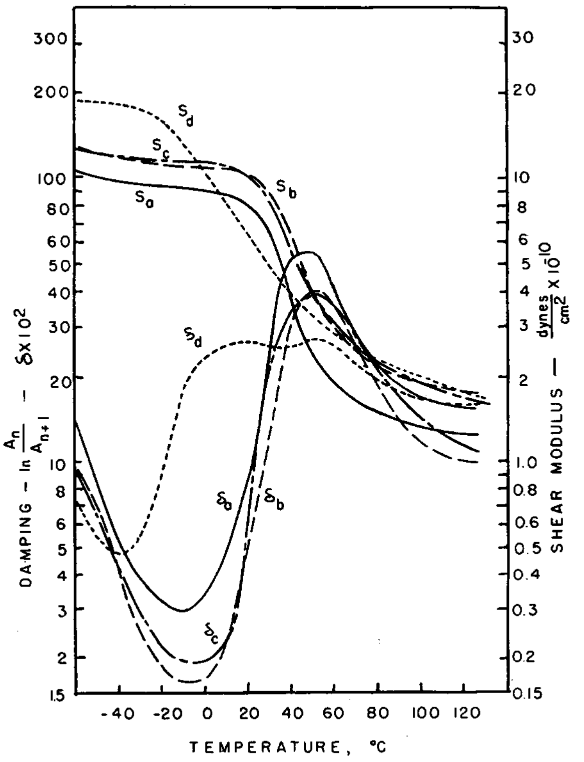

Fig. 3. Shear modulus and damping decrement as a function of temperature for injection-molded nylon 6 (Plaskon 8200) before and after various thermal treatments and steaming: (——) as molded: (– –) 17 hr. at 150°C.; (— – —) 17 hr. at 200°C.; (- -) 24 hr. at 120°C. steam.

on the few samples where variable periods were tried.

The data are summarized in Figures 1-3. For convenience in estimating the general effect of annealing, some reference data on shear modulus at three temperatures of testing are collected in Table II. The standard deviation for four samples increases from less than ±1 to almost ±3 units of the last significant figure cited in Table II in passing from −40 to 100°C. in Figures 1-3. In general, the greater the shear modulus, the less was the damping capacity of the sample, that is, the more brittle was the material.

ELECTRON MICROSCOPY

Most of the replica techniques commonly used on polymeric materials[10] either are insensitive to the fine detail of polyamide structure or, because of the poor wetting characteristics on nylon surfaces, tend to produce artifacts. Metal replicas, like the silver-silica technique,[10] are reliable but tedious. After considerable experimentation, the gelatin-silica replica technique[11] was adapted to nylon surfaces. On a few comparison samples this gave about the same results with a slight loss of detail as did the silver-silica technique. Some of the results of examination of samples are shown in the following series of figures. Only fracture surfaces were studied; samples were fractured with Izod Impact Tester on notched specimens cooled to −40°C. just before mounting in the sample holder.

In Figures 4-7 are shown the microstructures of fracture sections of injection-molded nylon 66 (duPont Zytel 101), as molded, after annealing at 150 and 200°C., and after steam treatment. Annealing increases the tendency toward a roughness type of fracture section. Steaming reduces coarse structure and smooths the fracture pattern.

Figures 8-11 show the microstructures of fracture sections of injection-molded nylon 610 (duPont Zytel 31), as molded, after annealing at 150 and 200°C., and after steaming. The same general effects of heating and steaming are observed as in Figures 1-4.

In Figures 12-15 are shown microstructures of fracture sections of injection-molded nylon 6

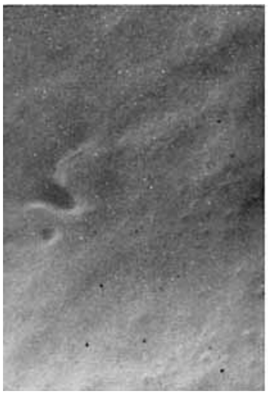
Fig. 4. As-molded Zytel 101; 38,300×.


Fig. 5. Annealed Zytel 101 (150°C.); 38,300×.

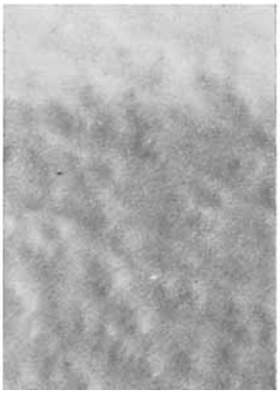
Fig. 6. Annealed Zytel 101 (200°C.); 38,300×.


Fig. 7. Steamed Zytel 101; 38,300×.

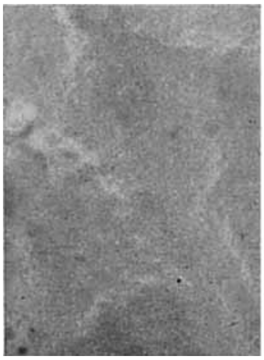
Fig. 8. As-molded Zytel 31; 15,500×.


Fig. 9. Annealed Zytel 31 (150°C.); 15,500×.

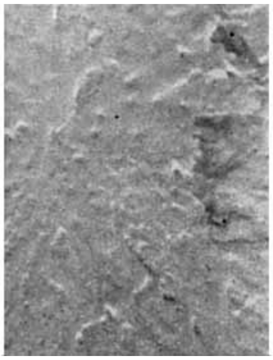
Fig. 10. Annealed Zytel 31 (200°C.); 15,500×.


Fig. 11. Steamed Zytel 31; 15,500×.

Fig. 12. As-molded Plaskon 8200; 38,300×.

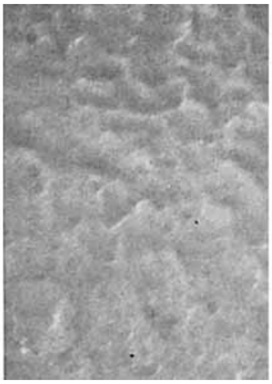

Fig. 13. Annealed Plaskon 8200 (150°C.); 38,300×.

Fig. 14. Annealed Plaskon 8200 (200°C.); 38,300×.

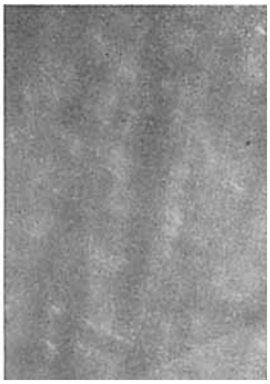

Fig. 15. Steamed Plaskon 8200; 38,300×.

(Plaskon 8200), as molded, after annealing at 150 and 200°C., and after steaming. The same general trend is seen as in the above series, except that there is relatively less difference between the fracture texture of molded and annealed samples. The tendency of steaming exposure to erase coarse structure patterns is more marked than with nylons 66 and 610.

DISCUSSION

In general, all the nylon samples at electron microscopy dimensions showed a cold-fracture pattern which our studies have shown will appear consistently only in polyphase polymer blends. This is probably due to nonuniform aggregation of ordered and disordered structures in the nylon or perhaps to the residual strains resulting from these thermal aging effects on adjacent domains wherein the polymer constituents have different properties. Annealing, even at 150°C., which is considerably below the melting point, has a marked stiffening effect upon the polymers and a noticeable effect on the fracture texture of the specimens. In fact, the annealing at lower temperature is more effective than that at temperatures close to the melting point in producing changes in mechanical properties. Greatest density changes, which may be due to increased crystallinity, occur only at the higher temperatures. It seems as though reorganization of the structure through annealing has more effect than does increased crystallinity in altering the mechanical properties. In fact, the room temperature-test data suggest that the specimens annealed at temperatures close to the melting point where increase of crystallinity should be greater are softer than those annealed at the lower temperature where the stiffening effect due to crystallization should be less.

Steaming the samples has a plasticizing effect on mechanical properties which coincides with a decrease of texture in the fracture patterns. The greater brittleness of the steamed samples at −40°C. suggests that either the steamed samples tend to retain more water, even after aging for several weeks in drying environments, or that low temperature properties are inferior for polymers which have a less ordered structure. Unfortunately, chemical determinations of moisture content were not made; hence the tempting explanation that low temperature embrittlement is due to freezing out of retained water was not proved. The possible greater importance of retained water content as compared to other factors is suggested by the observation that the properties of steam-aged and as-molded specimens of nylons 66 and 610 are nearly alike at the 100°C. temperature of test. This is less so for nylon 6. Possibly water was driven out of the steamed sample during the high temperature dynamic test. If this were so, the curves of Figures 1–3, when repeated on the steamed and as-molded specimens, should be brought together also in the other parts of the temperature scale in the second try. This did not prove to be the case. While properties at temperatures above 50°C. varied erratically in repeated cycles on the same specimens, the lower temperature portions of the curves (below 20°C.) continued to show considerable differences between steamed and as-molded specimens, both tending to be displaced somewhat in the directions of the first-run curves for dry-annealed specimens. Second- and third-run curves in the same specimens were poorly reproducible. Hence, beyond establishing the fact that the trend toward identity of 100°C. properties did not prevail at all temperatures, this issue was not pursued in detail. While variations in water content may contribute to modifying the aging history of the specimens, the effect seems to be more complex than can be explained simply as an instantaneous response to more or less plasticization with water.

References

1. Cooper, A. C., A. Keller, and J. R. Waring, *J. Polymer Sci.*, **11,** 215 (1953).
2. Fuller, C. S., W. O. Baker, and N. R. Pape, *J. Am. Chem. Soc.*, **62,** 3275 (1940).
3. Baker, W. O., and C. S. Fuller, *J. Am. Chem. Soc.*, **64,** 2399 (1942).
4. Meyer, K. H., *Natural and Synthetic High Polymers (High Polymer Series, IV)*, Interscience, New York, 1950, p. 267.
5. Langkammerer, C. M., and W. E. Cathin, *J. Polymer Sci.*, **3,** 305 (1948).
6. Keller, A., *Nature*, **169,** 913 (1952).
7. Starkweather, H. W., G. Moore, J. Hansen, R. Brooks, and T. Roder, *J. Polymer Sci.*, **21,** 189 (1956).
8. Nielsen, L. E., *Rev. Sci. Instr.*, **22,** 690 (1951).
9. Drummond, D. G., *The Practice of Electron Microscopy*, Royal Microscopical Soc., London, 1950.
10. Bobalek, E. G., L. R. Le Bras, A. S. Powell, and W. von Fischer, *Ind. Eng. Chem.*, **46,** 572 (1954).
11. Rochow, T. G., and F. G. Rowe, *Anal. Chem.*, **21,** 461 (1949).

Synopsis

The mechanical properties of injection-molded nylon 66, nylon 610, and nylon 6 can be altered significantly by steaming or heat-aging treatments which do not appear to be severe enough to cause density changes which would suggest much of a shift in the ratio of crystalline to mesomorphic polymer. However, some electron microscopy studies have demonstrated that such treatments are reflected markedly in the microstructure of fracture patterns on test bars broken at −40°C. The greater the change in microstructure, the greater was the residual effect of thermal or steam aging on the shear modulus and damping characteristics of the polymer. In general, dry annealing promoted embrittlement, particularly at low temperatures. Residual effects of steaming enhanced embrittlement at −40 and 100°C. but promoted softening at room temperature. The relative stability of room-temperature properties to dry annealing was greatest for nylon 66, and to steaming for nylon 6.

Résumé

On peut altérer d'une manière significative les propriétés mécaniques du nylon 6-6, 6-10 et 6 par l'action d'agents tels que la vapeur d'eau ou la chaleur. Ce traitement qui n'apparait pas assez sévère pour produire des changements de densité qui suggèreraient un changement considérable dans le rapport des parties cristallines aux parties amorphes du polymère. Cependant la microscopic électronique a démontré que de tels traitements se marquent sérieusement sur la microstructure des barres témoins brisées à −40°C. On constate qu'au plus grand changement de microstructure correspond le plus grand effet résiduel de ces agents sur le module de cisaillement et sur les propriétés hydroscopiques du polymère. En général le recuit en atmosphère sèche favorise la fragilité particulièrement aux basses températures. L'effet résiduel de la vapeur d'eau augmente la fragilité à −40 et à +100°C. mais favorise le ramollissement à la température de chambre. La stabilité relative des propriétés à température de chambre est la plus grande pour le nylon 6-6 avec recuit à sec et pour le nylon 6-10 chauffage au moyen de vapeur d'eau.

Zusammenfassung

Die mechanischen Eigenschaften von Spritzguss-Nylon 66, -Nylon 610 und -Nylon 6 können durch Behandeln mit Dampf oder durch Hitzealterung auch dann beträchtlich geändert werden, wenn diese Behandlung nicht scharf genug zu sein scheint, um Dichteänderungen hervorzurufen, die für eine starke Verschiebung des Verhältnisses von kristallinen zu mesomorphen Polymeren sprechen würden. Elektronenmikroskopische Untersuchungen haben aber gezeigt, dass sich eine solche Behandlung in der Mikrostruktur der Bruchformen von bei −40°C gebrochenen Teststäben widerspiegelt. Der bleibende Einfluss der Hitze-oder Dampfalterung auf den Scherungmodul und die Dämpfungscharakteristik des Polymeren war um so grösser, je grössere Änderungen der Mikrostruktur auftraten. Im allgemeinen führte eine trockene Temperung zu erhöhter Versprödung, besonders bei niedrigen Temperaturen. Die Dampfbehandlung lieferte als bleibenden Effekt eine Erhöhung der Versprödung bei −40 und 100°C, bewirkte aber eine Weichmachung bei Raumtemperatur. Die relative Beständigkeit der Raumtemperatur-Eigenschaften gegen trockene Temperung war bei Nylon 66 am grössten und diejenige gegen Dampfbehandlung bei Nylon 6.

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