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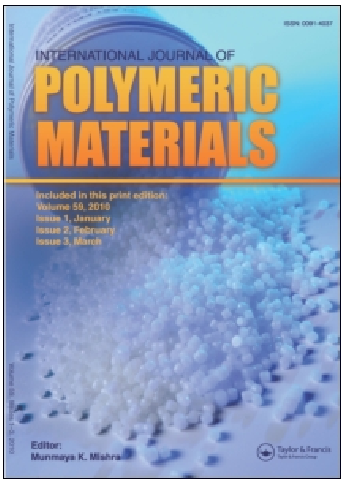

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Glass Transition Temperature and the Nature of the Amorphous Phase in Semicrystalline Polymers: Effects of Drawing, Annealing and Hydration in Polyamide 6

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To cite this Article Murthy, N. Sanjeeva(2001) 'Glass Transition Temperature and the Nature of the Amorphous Phase in Semicrystalline Polymers: Effects of Drawing, Annealing and Hydration in Polyamide 6', International Journal of Polymeric Materials, 50: 3, 429 — 444

To link to this Article: DOI: 10.1080/00914030108035118

URL: http://dx.doi.org/10.1080/00914030108035118

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Intern. J. Polymeric Mater., 2001, Vol. 50, pp. 429–444
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Glass Transition Temperature and the Nature of the Amorphous Phase in Semicrystalline Polymers: Effects of Drawing, Annealing and Hydration in Polyamide 6

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(Received 8 February 2001; In final form 12 February 2001)

The influence of the organization of the amorphous chains segments on the glass transition temperature (T_g) in semicrystalline polymers is analyzed by studying the effects of drawing, annealing and hydration in polyamide 6 fibers. We consider the role of three of the features of the amorphous phase: orientation (configurational entropy), density (free volume) and confinement (segmental mobility). Three classes of amorphous phases are identified; two of these are constrained in the intercrystalline regions, at the fold surfaces (between the lamellae within the lamellar stack) and at the stem surface (growth surface of the lamellae or between the fibrils). The third species is the bulk amorphous phase outside the lamellar stacks, and constitutes a large fraction of the amorphous phase especially at low crystallinities. Because the small fraction of the amorphous chain segments in the intercrystalline regions, and because they are in confined spaces, we suggest that these interlamellar and the interfibrillar components do not contribute significantly to the observed major glass transition peak. Rather, it is the amorphous region outside the lamellar stack that determines the T_g. T_g increases upon drawing and decreases upon annealing (heat setting). Our data suggest that orientation has a direct influence on T_g and can easily be measured whereas the influence of crystallinity is more complex. The influence of orientation of T_g can be understood in terms of a two T_g model in which the oriented amorphous component has a higher T_g than the unoriented component.

Keywords: Glass transition temperature; Amorphous phase; Polyamide

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INTRODUCTION

Glass transition temperature (T_g) is a fundamental parameter that is universally used to succinctly describe the essential characteristics of the amorphous phase (see *e.g.*, review in Ref. [1]). T_g is the temperature at which a liquid-like phase freezes into an amorphous solid during cooling, or as more commonly defined, the glassy phase becomes rubbery during heating. At T_g, or more precisely in the temperature range in the neighborhood of T_g, amorphous chain segments or structural units become mobile and are able to absorb energy. This is reflected in the changes in many of the properties near T_g, chief among them are the decrease in the modulus and the increase in the specific heat. It is obvious that T_g is of practical relevance as it determines the processing conditions and the end-use properties of polymers. T_g can be used for instance to follow the absorption or diffusion of host molecules even in semicrystalline polymers. External variables that affect the structural features that determine the T_g are of great interest.

While T_g is quite useful as a composite index, by itself it does not lead to further understanding that will enable the control of the morphology to achieve the desired performance. For this, we need to understand the changes in the organization of the amorphous phase that gives rise to the observed changes in T_g. We need to examine the relation between structure and the onset of molecular relaxations that occur at T_g, and use these results to understand the structural features such as crystallinity and orientation that influence the T_g. Here we consider the effects of orientation (drawing), heat-treatment (annealing) and the moisture (hydration).

EXPERIMENTAL PROCEDURES

Materials

Data from two sets of samples of PA6 fibers are reported in this study. One set was a series of fibers drawn to 1, 2.5, 3, 3.5, 4 and 4.5 times their length. A second set of fibers were a control PA6 fiber annealed (heat set) in dry (Suessen) and wet (Superba) conditions. Also included

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are previously published data on the effect of annealing from four commercial fibers (A-D) with different shrinkage behavior.

DSC Measurements

T_g measurements on polyamides are difficult to carry out by conventional differential scanning calorimetry (DSC) because water evaporation, and some times nylon crystallization, mask the features associated with T_g. Therefore, the T_g measurements were carried out on an oscillating DSC (ODSC) using Seiko's RDC 220 system. Data from about 10 mg of yarns were obtained at a fixed frequency of 0.01 Hz and a 10°C amplitude. A correction of +7°C, which was determined by comparing the ODSC T_g value with that determined by standard DSC, was applied to the data.

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X-ray Measurements

X-ray diffraction (XRD) data were collected on a Philips diffractometer in transmission geometry. A series of radial scans were collected at various azimuthal angles, as well as a "fast-rotational" scan intended to eliminate the effects of fiber orientation. These scans were profile fitted to crystalline and amorphous peaks to determine the crystallinity and orientation as described in detail in our earlier publication [2, 3]. Briefly, crystallinity is determined from the ratio of the area under the crystalline peaks to the total scattered intensity, and orientation is determined from the azimuthal width of the crystalline peak (for crystalline orientation) or the amorphous halo (for amorphous orientation).

Neutron Scattering

Small-angle neutron scattering (SANS) data were obtained fully hydrated fibers using D_2O as the contrasting agent. SANS measurements were carried out at the National Institute of Standards and Technology on their 10 m SANS instrument [4]. SANS data permit us to compare the morphology of wet fibers with T_g data obtained in the presence of moisture.

RESULTS

A typical DSC scan from a fiber (4.0 drawn and bone dry, *i.e.*, 0% humidity) is shown in Figure 1. Measurement of T_g from the inflexion point in the scan, *i.e.*, where the specific heat changes is illustrated in the figure. ODSC data show that T_g decreases from 55°C to −20°C in the presence of moisture. Figure 2 shows the variation in T_g with draw ratio in wet and dry fibers. The plot for the dry fibers shows that T_g does not change with the draw ratio. This is surprising because both the crystallinity and the orientation are increasing with draw ratio, and either of them would be expected to raise the T_g of the fibers. The expected increase in T_g is however seen in the wet samples at both 45% and 100% RH.

The variation in the T_g in fibers upon heat setting, *i.e.*, annealing, is given in Table I. The T_g decreases upon annealing. The table also gives the crystallinity, crystalline orientation and the amorphous orientation in these fibers. These data are excerpted from our earlier publications [2]. Wet (Superba) heat setting affects T_g more than dry (Suessen) heat setting [5].

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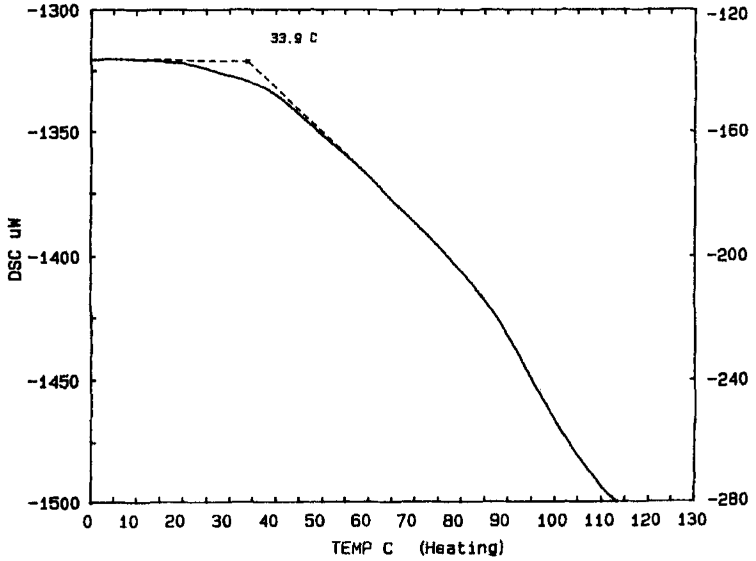

FIGURE 1 Typical DSC scan that is used in determining the T_g.

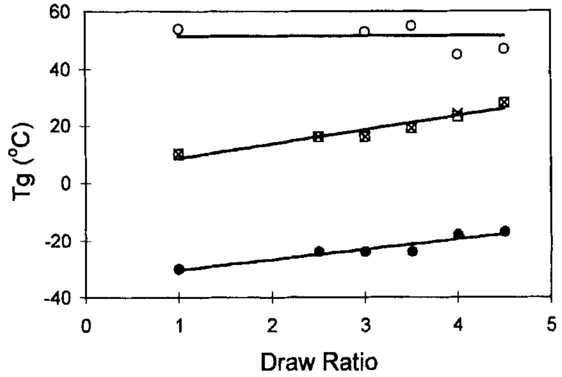

FIGURE 2 Variation in T_g with draw ratio for PA 6 at three levels of humidity. (a) Open circles – 0% from "bone dry" fibers. (b) Open squares – 45% humidity, and crosses – ambient conditions. (c) Filled Circles – at 100% humidity (soaked in water).

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The influence of crystallinity on T_g of the fibers in both the drawn and the annealed series is shown in Figure 3a [2, 5]. We see that crystallinity has no apparent effect on the T_g. Although one could argue that the decrease in orientation in the annealed fibers offsets the effect of increased crystallinity on T_g, in drawn fibers the crystallinity increases with orientation. Hence one would expect to see a much larger increase in T_g with crystallinity in the drawn fibers. But, we find that crystallinity has no influence on T_g.

The influence of amorphous orientation on T_g is shown in Figure 3b. It is difficult to achieve orientation without concomitant increase in crystallinity. However, on the basis of published results on nylon films with little or no orientation [6], it is possible to conclude that large part of the increase in T_g is due to increase in the orientation.

SANS data from a series of drawn fibers (same as the ones used in Fig. 2) and a fiber before and after heat setting (wet and dry process) are plotted in Figure 4 in the from of variation in T_g with lamellar spacing and lamellar peak intensity. Both the DSC and SANS in this figure are from fully hydrated (100% humidity) fibers, and hence allow unambiguous comparison of the relaxation behavior and morphology. The T_g appears to increase with decrease in lamellar intensity in both sets of fibers. However, while the T_g increases with lamellar spacing upon drawing, we see that it decreases with increase in lamellar spacing during annealing.

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TABLE I Effect of annealing (heat setting) on the glass transition temperature (T_g), crystallinity and orientation (crystalline and amorphous) in PA 6 fibers. Four fibers (A – D) with different shrinkages are listed below. NHS refers to the control or non-heat set fiber, and HS refers to the annealed or the heat set fiber

Fiber ID	*T_g (°C)*		*Crystallinity (%)*		*Crystalline orientation*		*Am. Orientation (Foa)*	
(% Shrinkage)	*NHS*	*HS*	*NHS*	*HS*	*NHS*	*HS*	*NHS*	*HS*
A (23%)	39	18	30	35	0.97	0.956	0.44	0.32
B (16%)	22	9	29	43	0.924	0.952	0.38	0.31
C (15%)	14	−6	24	42	0.918	0.934	0.35	0.26
D (9%)	14	−3	27	38	0.93	0.948	0.33	0.28

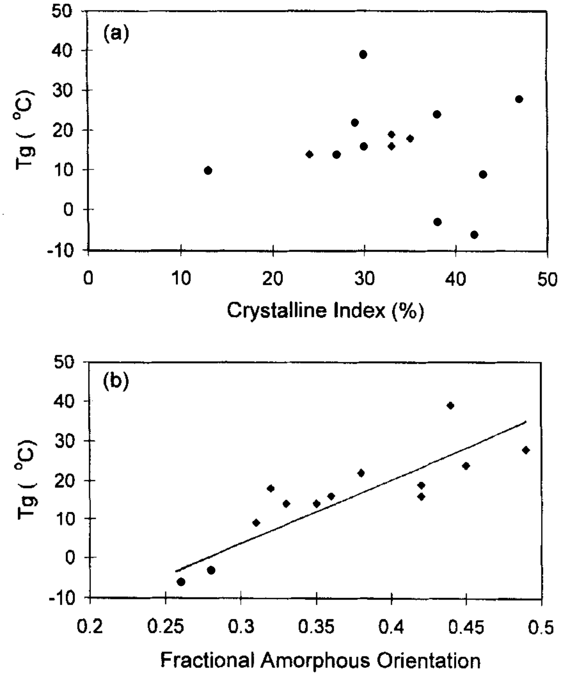

FIGURE 3 (a) Absence of correlation between T_g and crystallinity. (b) Correlation between T_g and fractional amorphous orientation.

DISCUSSION

It is known that T_g of a polymer depends on the constraints, or absence of it, to the mobility of the polymer chains. The correlations observed between T_g and the various structural features are usually explained by invoking such concepts as orientation, pinning and packing of the amorphous chain segments. T_g at the free surface of a polymer is lower than in the bulk [7], and the T_g of a polymer in confined spaces in the presence of interfacial interactions and at distances up to 15.0 nm [8]. A large variety of local structures between these two extremes are expected to be present in a typical polymer; accordingly, a polymer chain can experience a range of environments between these two extremes. The precise distribution is probably determined by the processes that shape the product into a fiber, film or

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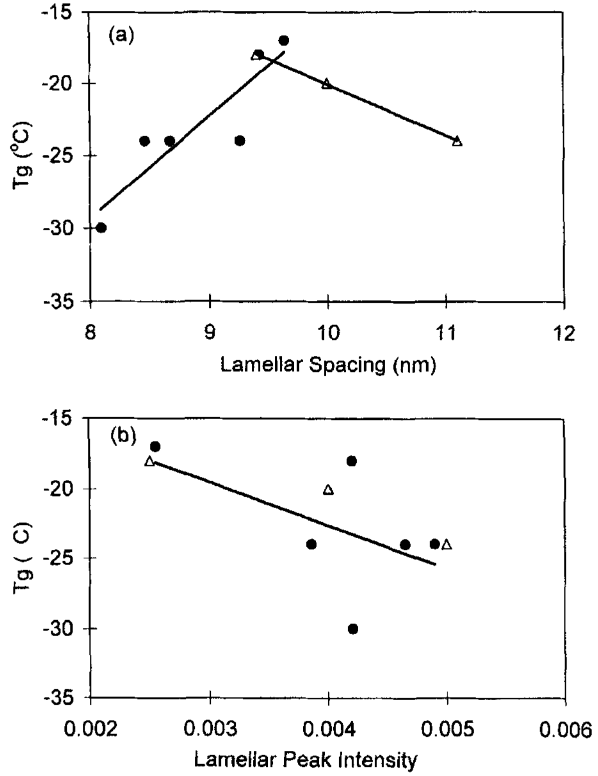

FIGURE 4 SANS data from drawn (filled circles) and annealed (open triangles). (a) T_g *vs.* lamellar spacing. Lamellar spacing increases with draw ratio, and upon annealing. (b) T_g *vs.* Lamellar peak intensity. The intensity decreases upon drawing and increases upon annealing.

a molded plastic. Thus, we can consider the relaxation of a fiber at T_g to be a superposition of many overlapping distributions or components. Our goal is to understand the influence of structure on T_g in the context of three common processes used in fiber manufacture namely drawing (stretching), heat setting (annealing) and dyeing (hydration).

Effects of Crystallinity

Crystalline regions in a semicrystalline polymers can be regarded as physical crosslinks that interact with many amorphous chain segments. Crystalline regions can thus greatly inhibit the motion of

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the amorphous chains tethered to or interacting with the crystal surfaces and therefore T_g is expected to increase with crystallinity. Although there are reports that support this supposition [1], there are also reports that indicate that T_g does not depend on the crystallinity per se [6]. Also, our data show that although the crystallinity increases during both drawing and annealing, the T_g increases only upon drawing (Fig. 2) but not upon annealing (Tab. I). The discrepancy in the reported influence of crystallinity on T_g could perhaps be because it is the surface area of crystals that interact with the amorphous chain segments that are important rather than the crystallinity by itself. Thus, in principle, the T_g of a polymer with large number of small crystallites could be higher than that of the polymer with higher crystallinity if this crystallinity is due to a small number of large crystals. Furthermore, the intercrystalline regions, which are affected by the crystallinity, may not play a role in the major glass transition relaxation that is usually reported in the literature. Thus, the crystallinity may not directly influence the T_g and the observed correlation between T_g, and crystallinity could be fortuitous.

Let us consider a typical PA with 35% crystallinity. If the lamellar spacing is 8 nm and the crystal height is 6 nm, then the crystallinity within the lamellar stack is 75%. Thus, 82% of the amorphous material is outside the lamellar stack and only 18% is between the fold surfaces of the lamellae [11]. It is unlikely that this small fraction would have a large influence on T_g. More importantly, these chain segments are confined in a small space ($\sim$2 nm) and strongly interact with the fold surface, and therefore are unable to relax at T_g [8]. It is the large fraction of the amorphous chain segments outside the lamellar matrix, between lamellar aggregates and spherulites that determine the T_g.

A fraction of the amorphous phase at the non-fold surfaces is between the growth surfaces or the stem surfaces of the lamellae that is usually referred to as interfibrillar spaces in drawn polymers/fibers (Fig. 5). When fibrillar aggregates are present, as indicated by the 5–7 nm equatorial spacing (fibrils are about 6 nm in diameter), the interfibrillar space is typically less than 2 nm [12, 13]. Similar observation have been made on the basis of recent high resolution SEM micrographs on fibers (private communication, H. Chang, DuPont Co.). In these instances, the amorphous component between

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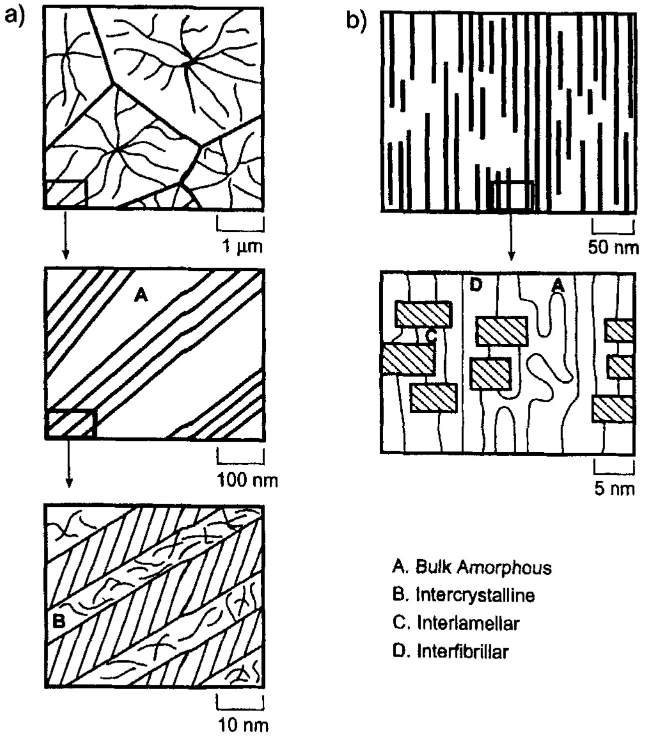

FIGURE 5 A model indicating the spatial distribution of the two confined amorphous species and the bulk (free) amorphous phase that for the amorphous "matrix" in semi-crystalline polymers. (a) Unoriented polymer with spherulitic morphology. Spherulites are shown as polygons in the top figure, the lamellar stacks are shown in the middle figure, and the interlamellar regions are shown in the bottom figure. (b) Oriented polymer with fibrillar morphology. Fibrils are shown as dark lines in the top figures, and the lamellae within the fibrils are shown in the bottom figure. Intercrystalline phase B in spherutic morphology and Interlamellar phase C in fibrillar morphology are essentially the same.

the fibrils constitutes ~20% of the total amorphous component; and this too is small compared to the almost 60% amorphous phase outside the lamellar/fibrillar matrix to affect the T_g, even if they could relax at T_g, which itself is unlikely. When the lateral extent of the amorphous domains is large (~5 nm), such as at the end of the fibrils (Fig. 5), then the amorphous chain segments in these regions can relax near T_g and affect the T_g. Obviously it is the non-intercrystalline amorphous component, *i.e.*, the chain segments that are neither in the interlamellar regions nor in the interfibrillar

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regions, but outside the lamellar/fibrillar matrix that are the major contributor to the T_g.

If intercrystalline regions would affect the T_g because of the cross-linking effect of the crystalline lamellae, then one would expect the lamellar spacing to have an effect on the T_g. But, whereas the lamellar spacing as well as the volume fraction of the interlamellar amorphous material (as indicated by increase in crystallinity) increases during both annealing and drawing [9], the T_g decreases during annealing and increases during drawing (Fig. 4a). Thus, it does not appear that the constrained amorphous phase in the interlamellar regions (next to the fold surface) influences the T_g. Furthermore, SAXS shows that interfibrillar space does not change significantly upon drawing (both the interfibrillar distance and the fibril diameter decrease upon drawing) [9, 10]. Hence, the interfibrillar (next to the stem surface) regions also do not appear to influence the T_g.

The above discussion leads us to invoke a three-phase model in which we have crystalline domains, bulk amorphous domain, and intercrystalline (confined) amorphous domains (Fig. 5) [14–16]. The confined phase could be in the interlamellar spaces (confined by the fold surfaces) and, in oriented systems, the interfibrillar spaces (confined by the stem surfaces or the growth surfaces). Intercrystalline domains, especially the ones between the fold surfaces are not capable of activation at T_g. The interfibrillar domains do participate in T_g if the spacing is larger than 2 nm. Scattering techniques follow only the intercrystalline species whereas the properties such as T_g's, strength and modulus are influenced by the bulk amorphous phase.

Effect of Orientation

Large changes in T_g caused by orientation have been previously reported [1, 4, 17]. For instance some of the data for PET show that whereas the T_g of a quenched sample is 79.7°C, increases to 81.3°C after cold crystallization at 172°C. In contrast, a biaxially oriented PET sample has a T_g of 103.3°C [17]. In our data we see that the increase in T_g upon drawing correlates with the increase in orientation (Fig. 3b), and the decrease in T_g upon annealing correlates with the decrease in orientation (Tab. I). The crystalline orientation is usually described by a single parameter, the degree of orientation (f_c), which

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represents an average of the angles between an unique axis (*e.g.*, chain-axis) within the crystallites and the draw direction. But the amorphous orientation requires two descriptors: one that denotes the fraction of the amorphous chain segments that are oriented (F_a), and the other that describes how well this anisotropic fraction is oriented with respect to the draw direction (f_a) [3]. Both these parameters, F_a and f_a, determine the T_g of the polymer [5]. The effect of orientation on T_g reflects the role of conformation and packing on the relaxation of the amorphous chain segments. The presence of unoriented domains is supported by the observation of unoriented deuterons and oriented deuterons in PA's in which the NH was converted to ND by exchanging with D_2O that preferentially diffuses only into the amorphous regions [18]. In 4.0 drawn fibers NMR estimates about 25% of ND is unoriented and 75% is oriented, although XRD data indicate that 55% of the amorphous phase to be unoriented and 45% oriented [2]. This difference could be because NMR calculations are based on a combination of orientation and the strength of H-D interaction between amide groups and water molecules.

The oriented amorphous phase has a higher T_g than the unoriented amorphous phase. The relaxation processes in highly drawn fibers are dominated by oriented components, and hence their T_g higher than undrawn and annealed fibers wherein the relaxation processes are dominated by unoriented components. This influence of orientation on T_g can be understood in terms of high-energy (temperature) required to activate the relaxation process in oriented chains. Alternatively, when a chain is extended from its unperturbed coil state, the configurational entropy decreases. Thus as the material is cooled, this entropy becomes zero at a higher temperature. If no such configurational entropy term is present, like in PVC, the T_g may indeed decrease with extension because of the stresses may activate molecular motions at a lower temperature to release strain [19]. Release of the stored strain energy upon annealing would be expected to raise the T_g, opposite to what we see in our data, and this is in fact observed in practice in PVC.

Effects of Drawing and Annealing

We have found that T_g increases upon drawing and decreases upon heat setting or annealing. The concept of oriented (anisotropic) and unoriented (isotropic) amorphous component is useful in understanding these changes in T_g. Increase in T_g during drawing is accompanied by an increase in amorphous (and crystalline) orientation. As the fiber is drawn, the unoriented amorphous fraction decreases (and this fraction eventually crystallizes), and the relaxation of the oriented amorphous components in drawn fibers occurs at a higher temperature and thus increase the T_g. Decrease in T_g during annealing is accompanied by a decrease in amorphous orientation (crystalline orientation increases in some instances and decrease in others). During annealing, as the oriented amorphous fraction crystallizes, the fraction of the unoriented, disordered fraction increases. The lower temperature for the relaxation of the unoriented amorphous chains lowers the T_g of the annealed fibers.

There are several reports that show that T_g increases with draw ratio [1] and orientation [17]. Our data in Figure 2 show that T_g does not change with draw ratio in bone-dry fibers, but increases with draw ratio in wet fibers both 45% RH and 100% RH. This suggests in undrawn fibers, the mostly unoriented amorphous phase absorbs more water and thus experiences a larger decrease in T_g. In the drawn fibers, the mostly oriented amorphous phase absorbs less water, and shows a smaller decrease in T_g. Thus, the increases T_g with draw ratio is a reflection of the amount of water absorbed by the amorphous phase, which in turn is a reflection of the orientation of the amorphous phase. If this oriented amorphous phase is constrained into a space $<2\,\text{nm}$, then they might not affect the T_g unless they are activated by a plasticizing agents such as water in polyamides.

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Hydration

Water acts as a plasticizer in nylons and reduces the T_g. It has been postulated that water inserts itself between C=O groups (strongly bound water) as well as between the NH and C=O groups (weaker bonding) on adjacent chains [20–24]. Additional water molecules, beyond about 1 water per two amide groups (0.5 H_2O per amide, or 50% saturation) results in the formation of water clusters which interact with the bound water molecules [23]. This model is supported by the observed steady decrease in T_g and Young's modulus towards a limiting value at about 5% wt (*cf.* 11% maximum water uptake), with little change with further increase in the water concentration [23, 24].

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^2H NMR indicates accordingly that the species at $>5\%$ water is isotropic and has a spin-lattice relaxation time (T_1) of 0.207 s, and comes off first during drying [18]. The second species with T_1 of 0.150 s is most intense in undrawn and 2.5 × fibers, is partially oriented, is accompanied by the decrease in the interlamellar intensity, and is more readily accessible than the interfibrillar domains. We attribute this second to bulk amorphous domains. The third species with a T_1 of 0.003 occurs first at a draw ratio of 3.0, is highly oriented, could represent confined intercrystalline domains, including interfibrillar domains.

The interfibrillar SANS intensity, and therefore the water in these domains, remains unchanged as a function of draw ratio of the fibers [4]. This supports our earlier contention that the amorphous chain segments in the interfibrillar regions may not contribute to the observed changes in T_g. Figure 4b shows that SANS lamellar intensity decreases upon drawing and increases upon heat setting. This change in the SANS intensity is due to the change in the accessibility of the interlamellar amorphous regions to water (D_2O), or the density of these interlamellar domains. Thus, the data in Figure 4b show that T_g increases as the interlamellar amorphous regions becomes more dense probably because of higher amorphous orientation in the drawn fibers and in fibers prior to annealing. However, it is possible that as the intercrystalline (thus including both interlamellar and interfibrillar) orientation is increasing, the orientation in the bulk amorphous phase is also increasing, and it is this bulk orientation that affects the T_g. The large decrease in T_g in both undrawn and annealed fibers due to water can be attributed to a large fraction of the unoriented bulk amorphous phase.

The increase in the length and diameter and the diameter of a swollen fiber is 7 and 2%, respectively for an undrawn fiber, the corresponding values for a drawn fiber are 2.7 and 2.6% [25]. The increase in the diameter, which is brought about by swelling of the interfibrillar amorphous phase, is about the same in both undrawn and drawn fibers indicating only minor changes in the organization of this phase upon drawing. Because the increase in the lamellar spacing upon hydration is $\sim 1\%$ [11], the large in increase in length in the undrawn fiber (about 5 times) cannot be accounted for the swelling of the interlamellar amorphous phase. Thus, there is a third species of the amorphous phase which either swells or transforms into oriented crystalline domains that brings about this increase in the fiber length.

CONCLUSION

We find that T_g does not always increase with crystallinity, but increases with orientation. The observed T_g is due to a distribution of relaxation processes, oriented amorphous segments relaxing at a higher temperature than those that have no orientation. This distribution occurs from the different classes of amorphous phases that are typically present in a polymer. Amorphous chain segments confined in the < 2 nm spaces between the crystalline regions do not contribute to T_g. The chain segments outside lamellar matrix, rather than those in the intercrystalline regions, determine the T_g. We suggest that changes such as decrease in orientation and crystallization of the oriented amorphous fraction occur not from the pool of amorphous domains in the interlamellar or interfibrillar spaces, but from the pool of amorphous phase outside the lamellar matrix. Crystallinity by itself has no effect because the amorphous regions within the lamellae do not contribute to T_g.

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References

[1] Aharoni, S. M. (1997). *Polym. Adv. Technol.*, **9**, 169.
[2] Murthy, N. S., Bray, R. G., Correale, S. T. and Moore, R. A. F. (1995). *Polymer*, **36**, 3863.
[3] Murthy, N. S., Minor, H., Bednarczyk, C. and Krimm, S. (1993). *Macromolecules*, **26**, 1712.
[4] Murthy, N. S. and Orts, W. J. (1994). *J. Polym. Sci. Polym. Phys.*, **32**, 2695.
[5] Murthy, N. S. (1997). *Text. Res. J.*, **67**, 511.
[6] Khanna, Y. P., Kuhn, W. P. and Sichina, W. P. (1995). *Macromolecules*, **28**, 2644.
[7] Forrest, J. A., Dalnoki-Veress, K., Stevens, J. R. and Dutcher, J. R. (1996). *Phys. Rev. Lett.*, **77**, 2002.
[8] Overney, R. M., Buenviaje, C., Luginbühl, R. and Dinelli, F. (2000). *J. Therm. Anal. Calorimetry*, **59**, 205.
[9] Murthy, N. S., Bednarczyk, C., Moore, R. A. F. and Grubb, D. T. (1996). *J. Polym. Sci. Polym. Phys.*, **34**, 821.
[10] Murthy, N. S., Grubb, D. T., Zero, K., Nelson, C. J. and Chen, G. (1998). *J. Appl. Polym. Sci.*, **70**, 2527.
[11] Murthy, N. S., Stamm, M., Sibilia, J. P. and Krimm, S. (1989). *Macromolecules*, **22**, 1261.

[12] Van Veld, R. D., Morris, G. and Billica, H. R. (1968). *J. Appl. Polym. Sci.*, **12**, 2709.
[13] Reimschuessel, A. C. and Prevorsek, D. C. (1976). *J. Polym. Sci. Polym. Phys.*, **14**, 485.
[14] Jin, X., Ellis, T. S. and Karasz, F. E. (1984). *J. Polym. Sci. Polym. Phys.*, **22**, 1701.
[15] Sauer, B. B. and Hsiao, B. S. (1995). *Polymer*, **36**, 2553.
[16] Vergelati, C., Imberly, A. and Perez, S. (1993). *Macromolecules*, **26**, 4420.
[17] Sichina, W. J. (1994). *American Lab.*, January, p. 46.
[18] Hutchison, J. L., Murthy, N. S. and Samulski, E. T. (1996). *Macromolecules*, **29**, 5551.
[19] Wetton, R. E. (1993). *Eur. Polym. J.*, **29**, 131.
[20] Pufrr, R. J. and Sebenda, J. (1967). *J. Polym. Sci.*, **C-16**, 79.
[21] Deopura, B. L., Sengupta, A. K. and Verma, A. (1983). *Polym. Commun.*, **24**, 287.
[22] Papir, Y. S., Kapur, S., Rogers, C. E. and Baer, E. (1972). *J. Polym. Sci. part A-2*, **10**, 1305.
[23] Bellinger, M. A., Ng, C.-W. A. and MacKnight, W. J. (1995). *Acta Polymer.*, **46**, 361.
[24] Reimschuessel, H. K. (1978). *J. Polym. Sci. Polym. Chem.*, **16**, 1229.
[25] Razumovskii, L. P., Markin, V. S. and Zaikov, G. Ye. (1985). *Polym. Sci. USSR*, **27**, 751.

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