

Correlation and Prediction of Polyamide Glass Transitions

RALPH G. BEAMAN, *Pioneering Research Division, Textile Fibers Department, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware*

Synopsis

A simple scheme for the prediction of glass transition temperatures based on diamine and diacid component part contributions is applied to data for 19 interrelated polyamides. The new results, in conjunction with many prior determinations, lead to the assignment of $65 \pm 20^\circ\text{C}$. for the glass transition of 6-6 polyamide, contrary to published suggestions that the value might well be -65°C .

In a recent paper¹ it was stated that the glass transition temperature, T_g , of 6-6 polyamide might well be about -65°C . This value is inconsistent with previous literature values which indicate a T_g in the range 45 – 85°C ., any specific value depending, of course, on sample, method, and interpretation. In both published and unpublished work there have been direct measurements by nearly a dozen different methods, numerous observations of property and processing changes with temperature known to be associated with T_g , and correlated measurements on many other polyamides.

We shall elaborate on this last point by presenting a simple yet powerful method for correlation and prediction of T_g .

The glass transition of a polymer is completely determined by its structure, which in turn, is a direct result of the structures of its component parts. For polyamides we then assign a contribution to T_g for each diamine and dibasic acid (or amino acid) as it appears in polymers. This does not mean that a component has a T_g value but rather with its complementary reagent it has an effect on T_g in a polymer.

Consider a polyamide X-Y with T_g of 100°C . As a reference point to which all other numbers are related any component may arbitrarily be assigned any number. For example, if we choose X and a number of 0, then Y must have a number of 200 to give the average of 100 for the polymer. From known T_g 's for W-Y and X-Z, numbers for W and Z are deduced. These then allow a prediction of T_g for W-Z. The equation is $T_g = 0.5$ (diamine number + diacid number).

From the data of Temin,¹ it is instructive to choose as a base point the polyamide F-F (see Table I for explanation of codes) with a T_g of 165°C . From symmetry considerations we select a number of 165 for one compo-

TABLE I
 Polyamide Glass Transitions^a

Diamine ^b (Number)	Dibasic acids ^c (Number)				
	10 (5)	6 (75)	F (165)	D (165)	I (185)
	Observed and (Calculated) T_g , °C.				
6	30, ^d 50 ^e	45-85 ^f	122	127	130
(75)	(40)	(75)	(120)	(120)	(130)
MXD	—	73	150	159	165
(145)	(75)	(110)	(155)	(155)	(165)
F	85	120	165	165	175
(165)	(85)	(120)	(165)	(165)	(175)
Pip	82 ^g	126 ^h	145	193	192
(200)	(102)	(137)	(182)	(182)	(192)

^a Observed data from Temin¹ unless otherwise noted.

^b Diamines: 6 = hexamethylene; MXD = *m*-xylylene; F = fluorene-9,9-dipropyl; Pip = piperazine.

^c Diacids: 10 = sebacic; 6 = adipic; F = fluorene-9,9-dipropionic; D = diphenic; I = isophthalic.

^d Data of Beaman and Cramer.²

^e Data of Tippetts and Zimmerman.³

^f For leading references, see Temin.¹

^g Data of Flory et al.⁴

^h Data of Moseley and Parrish.⁵

ment, giving 165 for the other. From the T_g for the polymer 6-F we then deduce a number of about 75 for 6 diamine. Since structurally, F diamine is related to F diacid as 6 diamine is related to 6 diacid, as a first approximation we predict 75 for 6 diacid and hence 75°C. for 6-6. This is in excellent agreement with observed values. Thus we could predict T_g for 6-6 with no prior knowledge of any adipic acid polyamide.

However, it is best to assign numbers from observed T_g 's and then correlate these with structure. We can crosscheck this number for 6 diacid with F-6, which gives both predicted and observed values of 120°C. Using the other F diamine polymers and the I diacid polymers, we complete the numbers shown in Table I. Eight known T_g 's are used to predict twelve new T_g 's. The effect of structural variations on T_g is readily discernible from the component numbers assigned.

Hayes⁶ has proposed a semiempirical method for prediction of T_g for polymers of all classes based on a similar approach of component part contributions. He assigns both a bonding or molar cohesive energy factor, H_c , and a stiffness or degree of freedom factor, n , for atomic groupings. These factors are summed for all parts of the repeat unit and T_g (°K.) obtained from the equation.

$$H_c = 0.5nRT_g - 25n$$

The assignment of n values requires an arbitrary set of rules, H_c values still require reference polymers, and, as Hayes points out, interaction between

groups can result in considerable error. Our method, while more restricted in application, avoids the difficulties and further gives predictions by simple mental calculation rather than by pencil-and-paper arithmetic manipulation.

We have found that the method as outlined works equally well for copolymers (mole per cent basis) and, without refinements (to take into account the effect of totally different environments for the same component), generally can be used to predict T_g within 25°C. The two cases (MXD-6 and Pip-F) which deviate from predictions by 37°C. are slightly out of line and may well result from a combination of too high numbers assigned to the diamines and too low values in the observed determinations.

A value of -65°C. for 6-6 would represent a deviation of 140°C. from that predicted. The reference⁷ cited for -65°C. shows only a minor movement of the penetrometer needle at the low temperature, the major change being near 50°C., the higher temperature being "the temperature of the viscous flow of the amorphous phase." We feel there has been a misuse of the term "glass transition" for the -65°C. effect, prompted by the desire to set T_g below the crystallization temperature. The question has also been considered by Boyer,⁸ who concluded that a value of about 50°C. was consistent with all observations except crystallization temperature. The point now appears to be resolved by the recent work of Magill,⁹ who found a maximum crystallization rate at 141°C. with a reference temperature (minimum temperature, often associated with T_g) of 45 or 61°C., depending on the rate equation used.

It is of interest to note that the two-thirds rule^{10,11} relating T_g to crystalline melting point predicts 81°C. for the T_g of 6-6. A value of 71°C. is consistent with the elegant empirical relation of Lewis¹² relating frequency dependence of mechanical loss for polymers. These and the majority of other reports, as well as the method of prediction presented here, show $65 \pm 20^\circ\text{C.}$ for the T_g of 6-6.

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Résumé

Un simple schéma permettant de prédire les températures vitreuses sur la base des contributions des composants diamine et diacide a été appliqué aux données sur 19 polyamides reliés entre eux. Ces nouveaux résultats en fonction avec des déterminations antérieures amènent à attribuer comme transition vitreuse du polyamide-6-6, une température de $65 \pm 20^\circ\text{C}$ contrairement aux suggestions publiées qui proosaient une valeur de -65°C .

Zusammenfassung

Ein einfaches, auf den Beiträgen der Anteile an Diamin- und Dikarbonsäurekomponenten beruhendes Schema für die Voraussage von Glasumwandlungstemperaturen wird auf die Daten für 19 verwandte Polyamide angewendet. Die neuen Ergebnisse führen gemeinsam mit vielen früheren Bestimmungen zur Annahme eines Werts von $65-20^\circ\text{C}$ für die Glasumwandlung von 6-6-Polyamid im Gegensatz zu veröffentlichten Vorschlägen, welche einen Wert von -65°C für möglich halten.

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