Remarks on the α and β transitions in swollen polyamides

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The glass transition (α) and secondary transition (β) are compared in various aliphatic polyamides swollen by water, alcohol and acid. For all these polymer–solvent systems, the evolution of the temperature T_α with the equilibrium sorption ratio presents two regimes. In the low-concentration regime, the dependence of T_α on the number n of absorbed solvent molecules per accessible amide group follows a master curve independent of the nature of the system. No master curve is, however, observed for the β transition. In the second regime, above a critical ratio n^* dependent on the nature of both the solvent and the polymer, T_α levels off, and the maximum concentration of absorbed solvent is proportional to n^*. These effects are explained in terms of solvent clustering around the amide groups.

(Keywords: polyamide; water absorption; glass transition)

INTRODUCTION

When the properties of the glass (α) and secondary (β, γ) transitions are analysed, it is apparent that there are major differences between polymers with interchain hydrogen bonding such as polyamides (PAs) and those which have only van der Waals interactions. It has been noted by numerous authors[1–15] that the glass-transition-temperature depression caused by polar plasticizers such as water and alcohols does not follow the empirical Fox law or semiempirical laws based on the free-volume concept[16–18]. This is not surprising since additivity of free volume is not observed[3,7]. The same conclusions have been drawn for cellulose and cellulose ester systems swollen by water[19–21]. In general, one can conclude that, for polymers having hydrophilic groups that are able to establish hydrogen bonding with polar solvents, the variation of T_α with the sorption ratio is greater than that predicted by the empirical laws.

The aim of this paper is to compare the dependence of the glass (α) and secondary (β) transitions of different aliphatic PAs on the solvent concentration at room temperature, to discuss the nature of the so-called states of the solvent in the different regimes of absorption, and to show that clustering of water molecules around the amide group can be deduced from the behaviour of the α and β transitions.

THE α TRANSITION

The value of the glass transition temperature T_α determined by mechanical and dielectric measurements depends on the frequency. Comparison must, therefore, be made at the same frequency. In most published works on PA, the glass temperature is obtained by d.m.t.a. (dynamical mechanical thermal analysis). In this paper, we compare the T_α values of PA systems obtained by d.m.t.a. at 1 Hz.

Figure 1 gives the dependence of the glass transition temperature T_α on the equilibrium sorption ratio S for various polyamides, PA6, PA6,6, PA11 and PA12, swollen by water[3–14], phenol[12] and formic acid[15]. S is defined as the increase of mass $(m-m_0)$ of the swollen material divided by the mass m_0 of the unswollen material. The characteristics of these polymer–solvent systems are given in *Table 1*. It is clear that, for any system, two regimes can be distinguished: T_α decreases linearly with the sorption ratio for low solvent content, and levels off at high solvent uptake. This behaviour was first noted by Kettle[7] for PA6 swollen by water. The main effect of polar solvents, as reported by many workers, is to break up the amide–amide interchain bonding, so that solvent–PA bonds are established. If one assumes that these interchain hydrogen bonds are equivalent to crosslinking in polymers that contain only van der Waals interactions, then the number of equivalent crosslinks should control the glass transition temperature.

For that reason, the data of *Figure 1* have been replotted in *Figure 2* as functions of the number n of absorbed solvent molecules per amide group in the amorphous phase. The crystallinity α_c has been taken into account. In each system the crystallinity is constant, between 30 and 46%, except for the system PA11–formic acid, where a continuous decrease of the crystallinity with increasing solvent content is reported[15]. One observes again two domains of variation for each swollen system: T_α decreases linearly with n below a critical concentration n^*, and reaches a constant value above n^*. The critical ratio n^* separating the two domains and the T_α value at saturation depends on the nature of both the polymer and the solvent. The existence of a master curve for the evolution of T_α with n is apparent in the first regime. The pure PAs have T_α values that do not vary significantly with the number of CH_2 groups between amide groups[6]. We will not, therefore, differentiate between these different master curves because the variation of T_α with n is much more important than that with the nature of the PA. The

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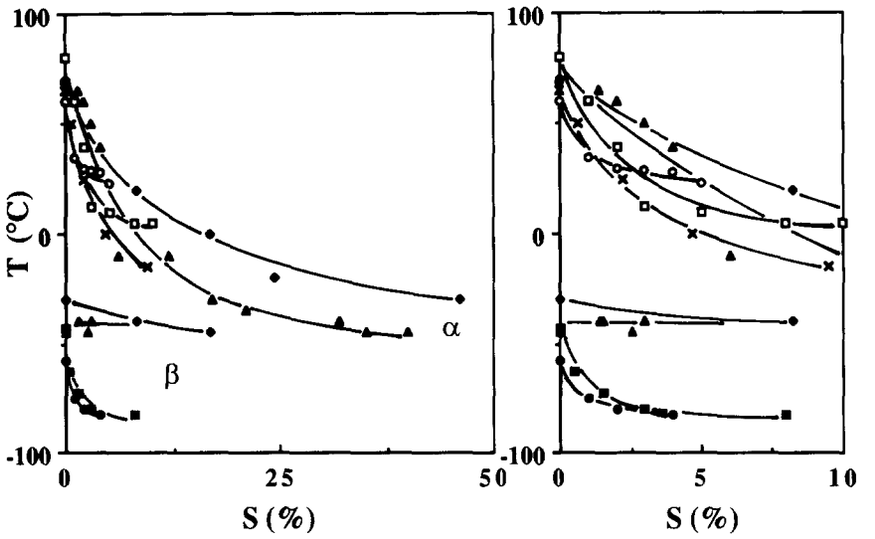

Figure 1 Transition temperatures T_α and T_β of various polyamide–solvent systems, as functions of the equilibrium swelling ratio S. PA6–water[4,6,8]: T_α (□), T_β (■); PA12–water[6,10]: T_α (○), T_β (●); PA6,6–water[1,13]: T_α (×); PA6–phenol[12]: T_α (◇), T_β (◆); PA11–formic acid[15]: T_α (△), T_β (▲)

Table 1 Characteristics of PA swelling by solvents

PA	α_c[a] (%)	Solvent	χ_{12}[b]	n^*[e]	n_m[f]	$T_{\alpha,sat}$[g] (°C)
PA12[6,10]	30	H_2O	2.1[c]	0.2	0.8	20
PA6[4,6,8]	37	H_2O	1.9[c]	0.3	0.9	5
PA6,6[1,13]	46	H_2O	1.4[c]	0.3	1.1	−15
PA6[12]	37	Phenol	0.7[d]	0.4	0.9	−30
PA11[15]	23	HCOOH (90%)	0.6[d]	0.6	3.2	−50

[a] Crystallinity ratio of PA determined by d.s.c. or density (see table 2 of ref. 14)
[b] PA–solvent interaction parameter
[c] Measured
[d] Calculated (ref. 17)
[e] Number of absorbed solvent molecules per amide group in the amorphous phase, determined by the intersection of the tangents at $n=0$ and $n=n_m$ of the $T(n)$ curves
[f] maximum number of absorbed solvent molecules per amide unit in the amorphous phase of PA swollen in water at room temperature
[g] T_α at saturation ($n=n_m$)

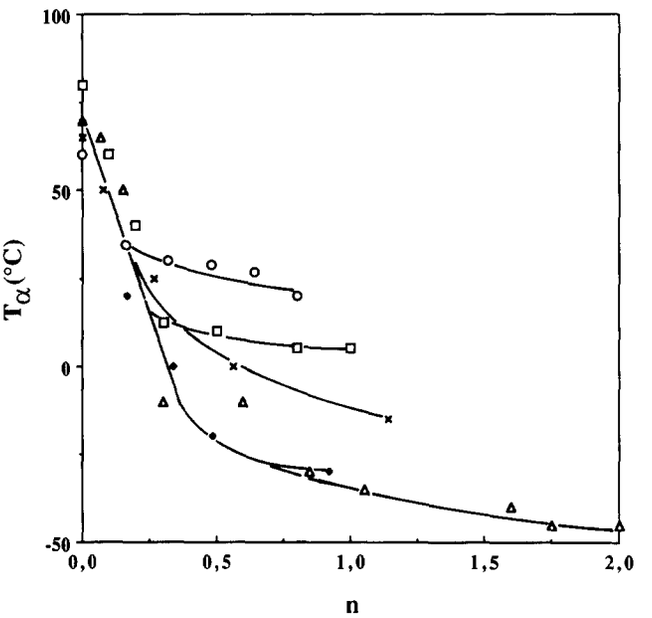

Figure 2 Glas transition temperature T_α of polymer–solvent systems, as a function of the number n of solvent molecules absorbed per accessible amide group in the amorphous phase. For each system, a critical ratio n^* can be defined: $T_\alpha(n)$ follows a master curve below n^*, and levels off above n^*

existence of such a master curve for $n<n^*$ indicates clearly that all the solvent molecules bare bound to the amide groups in a similar manner independent of the nature of the aliphatic PA.

Conformation calculations show that ideal chains of polyethylene (PE) and PA have similar rigidity[22] and, therefore, one would expect that both materials in the amorphous state would have glass transition temperatures of the same order. The higher glass transition temperature of PA can be explained by the effect of crosslinking resulting from amide–amide hydrogen bonding.

It is important to note that the extrapolation $T_\alpha=-150$°C for $n=1$ is of the order of magnitude of the glass transition temperatures T_g of PE (−125°C)[22] and of water (−135°C)[23–25]. This confirms that (hypothetical) completely amorphous PA chains, completely surrounded by a water layer to prevent interchain interactions, would be similar to ideal PE chains as far as the rigidity and the glass transition are concerned.

By analogy with crosslinked polymers[17], where $(1-n)$ would be the degree of crosslinking, one can express the lowering of T_α by the relation:

$$T_\alpha = T_\alpha^\circ - kn \qquad (n<n^*)$$

where T_α° is the T_α of the pure polymer without interaction. The constant k expresses the ability of the crosslinks to suppress the long-range movements of the chains; it does not vary with the nature of the PA and the solvent in the low-concentration regime.

Above the critical ratio n^*, the additional solvent molecules do not change the glass transition temperature significantly. One can suppose that, at n^*, certain accessible amide groups of the chains are bound to one solvent molecule, and then each additional solvent molecule ($n>n^*$) is sorbed on these same amide sites, which are already bound to a solvent molecule. This effect of solvent clustering explains why the above relation then

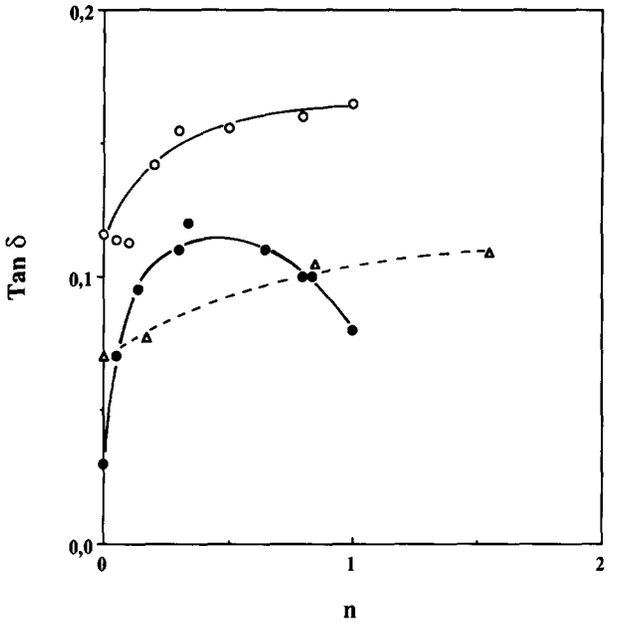

Figure 3 Intensities of the α (○) and β (●) peaks observed by d.m.t.a. at 1 Hz for the PA6–water system[4,6,8], as functions of the number n of solvent molecules per amide group. The broken curve represents the intensity of the α transition (△) for the PA11–formic acid system[15]

no longer holds. One must ask now what is the process that limits the size of these clusters.

An amide group can be bound to three water molecules: NH and CO groups can hydrogen bond with, respectively, one and two water molecules. Diffusion and viscosity measurements on mixtures of low-molecular-weight amides and water (and also in other non-electrolyte binary systems) show maxima when the mole ratio water/amide is equal to 3. This abnormal behaviour (non-ideal solution) has been observed by various authors[25,26]. Bezrukov[25] has interpreted this effect as being due to the formation of clusters of three bound water molecules per amide group. If one assumes that similar effects exist in PA, one would expect the maximum amount of absorbed water, n_m, to be three times the critical amount n^* necessary to bind all the accessible amide sites. *Figure 3* and *Table 1* show that this relationship, $n_m \approx 3n^*$, is observed for the PA–water systems. It would be interesting to check if such an equivalent law is observed for PA swollen by other solvents (alcohols for example).

It is important to understand why all the amide groups in the amorphous phase of PA systems are not accessible to water molecules ($n^* < 1$). *Table 1* shows the influence of the chemical affinity of the solvent for the polymer on the n^* and n_m values via the Flory–Huggins parameter χ_{12}. As the polymer and the solvent have similar polarities, the interaction parameters for the PA6–phenol and PA11–formic acid systems have been estimated by the following equation[17]:

$$\chi_{12} = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 + \chi_S$$

where V_1 is the molar volume of the solvent, δ_1 and δ_2 are the solubility parameters of, respectively, the solvent and the polymer, and χ_S is the entropic correction term ($\chi_S \sim 0.3$). For other systems, χ_{12} was taken from the literature[3,17]. Despite the uncertainty in the experimental and calculated values of χ_{12}, one can conclude that the critical ratio n^* increases when the interaction parameter decreases; n^* and therefore the maximum swelling ratio (n_m) is obviously controlled by the interaction parameter χ_{12}.

Finally it must be stressed that in the PA–water systems the notion of crystallizable and non-crystallizable water is not relevant. Water cannot crystallize because the polymer–water system is frozen in the amorphous state at T_g before passing through the crystallization temperature T_c of water ($T_g > T_c$).

THE β TRANSITION

From *Figure 1*, it is clear that T_β does not follow a master curve independent of the nature of the solvent. For good solvents such as phenol[12], formic acid[15] and butylbenzene[21], T_β does not vary with the solvent concentration. In these systems, the α and β relaxation peaks merge together when the solvent concentration increases. This effect rules out any precise determination of the variation of temperature and intensity of relaxation with the ratio n.

For PA–water systems, T_β decreases with concentration, as has been reported by many authors[1–14]. The decrease is faster for PA12 than for PA6. When plotted as a function of n, the two curves are superimposed. In these systems, an important difference between the α and β relaxations must be noted. The amplitude Δ_α of the α transition increases slowly with n in the first regime (15% variation) and then remains constant in the second regime above n^*. The amplitude Δ_β of the β transition increases (by an order of magnitude) and then decreases above n^*. *Figure 3* shows these variations for PA6[4,6,8]. Similar curves have previously been obtained for polypeptides (collagen, elastin and polyproline) by Hiltner[11]. These bipolymers can absorb a great amount of water ($c > 100\%$) and the $T_\beta(c)$ curves present a well defined maximum for a critical concentration c^* of water. The crystallinity of these materials is not known. Consequently, it is not possible to calculate for these materials the ratio n^* of water molecules per amide group (or polar group) of the chain.

We consider that the β transition is due to the mobility of water molecules and chain ends. According to some authors[6,9,14] the β peak disappears when the polymer is completely dried. According to other authors, the transition is partially due to the presence of low-molecular-weight PA chains. Annealing just below the melting point, under vacuum, increases the molecular weight of the chains via polycondensation reactions. For this type of material, the β peak disappears completely[14].

The origin of the β transition in dried PA is not completely understood. This mobility involves the breaking of hydrogen bonds. In the low-concentration regime, these entities being non-correlated (without interaction), the amplitude of the β relaxation is therefore proportional to the concentration of mobile entities.

Above n^*, if clusters are formed, the movement of the water molecules cannot be considered as independent; the intensity Δ_β would no longer be proportional to n. It has been reported by Kapur *et al.*[9] that PA6 swollen at 2.5% of water has a β transition whose characteristics (temperature and amplitude) are very similar to those of pure ice[27,28]. Therefore, if the material absorbed a great amount of water, the limit of Δ_β would be 2×10^{-3} times

the observed value for pure ice[17], much lower than the value of pure PA. This explains (qualitatively) why Δ_β decreases when the concentration of water increases in the second regime.

SUMMARIZING DISCUSSION

The characteristics (temperature and amplitude) of both relaxations, α and β, in PA–solvent systems show that there are two different regimes of absorption.

In the low-concentration regime, the linear decrease of T_α with the solvent concentration is interpreted as being due to the progressive disruption of the amide–amide interactions (equivalent to crosslinks) by solvent molecules. The number of disrupted amide–amide bridges depends on the solvent mole fraction, and all the PA–solvent systems display the same master curve $T_\alpha(n)$. In this regime $T_\beta(n)$ does not follow a master curve independent of the nature of the solvent, indicating that this transition is essentially due to the water molecules, the temperature and activation energies of the β transition in PA and in pure ice being of the same order of magnitude[9].

In the second regime, the constancy of T_α and T_β, and the maximum for the amplitude Δ_β, are interpreted as being due to the clustering of additional solvent molecules. The critical ratio of solvent molecules per amide group, n^*, separating the two regimes, is not an integer, but is a decreasing function of the polymer–solvent interaction parameter χ_{12}. The maximum mole ratio n_m of absorbed water molecules (the cluster size) is about three times the critical ratio n^*. In non-ideal aqueous solutions of amide, water clustering of this type has been proposed to explain the variations of the viscosity and of the diffusion constant with concentration[25,26].

Zimm[29] has shown that cluster sizes for solvents sorbed in polymers can be calculated from sorption isotherms. Following this approach, Starkweather[30] calculated the degree of water clustering of PA6,6; at 100% relative humidity, the number of water molecules in a cluster is about 2.5, not far from the value $n_m/n^* \approx 3$ deduced from the variation of T_α and T_β with n. Puffr *et al.*[5], using the same approach, found that PA6 and low-molecular-weight amides exhibit cluster sizes of the same order of magnitude and varying in the same way with the relative humidity; at 100% relative humidity, the clusters again consist of three water molecules.

Finally, in the literature, the distinction is often made between tightly and loosely bound water (and other solvents) in polymers able to establish hydrogen bonding with the solvent. These terms are probably misleading. In both high- and low-concentration regimes, all water molecules are bound in the same way to the amide groups. In the second regime, two types of relaxation times or diffusion times must be considered: the first is related to the jump of a water molecule from one amide site to a next, while the second is linked to the jump of a water molecule within a cluster. This latter process involves the phenomenon of H and O atom exchange between water molecules of the same cluster, which is the β process observed in ice. This interpretation is consistent with the n.m.r. studies on PA, poly(vinyl alcohol) (PVA) and cellulose–water systems at room temperature, which are interpreted in terms of mobile and less-mobile water[31–35]. Obviously, it should be of the greatest interest to pursue n.m.r. studies at lower temperatures, above and below the β transition temperature, to confirm this interpretation.

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