Moisture-Induced Plasticization of Amorphous Polyamides and Their Blends

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Synopsis

The moisture-induced plasticization of some amorphous polyamides in pure and blended form has been determined by calorimetric methods. The compositional dependence of the glass transition temperature of these polymer-diluent systems has been adequately accounted for using an existing predictive expression derived from both a conformational entropy and a thermodynamic treatment of the glass transition phenomenon. The success of this approach to account for the behavior of amorphous polyamide blends containing hydrophobic and hydrophilic constituents exemplifies the importance of compositional parameters in determining the overall response of morphologically complex hydrophilic polymers. The results add further credence to the simple plasticizing action of water in polar polymers irrespective of their chemical and physical constitution.

INTRODUCTION

The sustained incursion of polymeric materials into demanding applications necessitates increased vigilance with regard to their long-term behavior and durability. The glass transition temperature (T_g) often denotes a temperature threshold of utility marked by a precipitous change in some mechanical properties (e.g., modulus). This is particularly true for completely amorphous materials, and any agent, for example water, which can induce a substantial reduction of T_g requires special consideration. In this context the ubiquitous presence of moisture and the hydrophilic nature of many polymers is of considerable importance. Therefore it is often useful to know, a priori, how a hydrophilic polymer responds in a humid environment. These concerns are manifest by only a scant inspection of recent literature detailing a continued interest in the interactions of hydrophilic polymers with water.[1-4]

The polar nature of water, and the chemical functionalities often present in polymers in which water acts as a plasticizer, has often been the source of speculation with regard to the role of water–polymer interactions in the depression of T_g in these polymers.[2,5-7] Typically, water acting as a plasticizer at low concentration (1% by wt) can induce a 15–20°C reduction of T_g compared to a value of 4–5°C for common polymers plasticized by organic diluents. Discussion of observed behavior has sometimes centered on the "disruptive" potential of water molecules in hydrogen-bonded environments and the possibility that water molecules may exist in "free" or "bound" states within a polar polymer matrix.[2,5,6,8,9] It has also been demonstrated, however, that water has an effective but rational plasticizing action in hydrophilic polymers without resorting to the imposition of "disruptive" polymer-diluent interactions,[10] or the effects alluded to above. Similarly sub-T_g studies[11,12]

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have also indicated that water interacts in a simple and homogeneous manner with polar polymers in which it is soluble.

One of the supporting arguments from the aforementioned studies relies on the application of a theoretical description of the composition-dependent T_g in polymer-diluent binary systems to account successfully for observed behavior. Similar treatment of plasticization data from nonpolar polymer-diluent systems[13-15] has also provided good agreement between theory and experiment and therefore suggests a more universal application of this theoretical treatment. The expression used has been derived from a number of sources[16-18] and requires only a knowledge of the pure component thermal properties; T_g and the incremental change in heat capacity, ΔC_p, at T_g. However, the success of this type of approach in accounting for the water-induced plasticization of semicrystalline polyamides is compromised by the role of morphology.[19,20] Only by recognizing the importance of crystallinity as an influence on measured thermal properties and the distribution of plasticizer molecules within the accessible regions of a semicrystalline polymer is it possible, to some extent, to reconcile theory with experimental results. In search of further evidence that morphologically complex hydrophilic polymers containing polar functionalities are plasticized by water in a simple homogeneous manner, it would be instructive to examine amorphous polyamides in morphologies which are more clearly defined than those of semicrystalline polyamides. This would provide a firm basis from which to interpret the plasticization behavior of their morphologically complex counterpart, the semicrystalline polyamides. This study was undertaken in part to substantiate this approach to the effect of water on polar polymers irrespective of their chemical and physical constitution and to clarify the role of morphology in polymer-diluent interactions.

THEORY

Predictive treatments of the compositional dependence of the glass transition temperature in miscible polymeric binary systems have received considerable attention and have relied on a number of theoretical and phenomenological descriptions of the glass transition phenomenon. For polymer-diluent systems Kelly and Bueche[21] derived an expression based on an iso-free volume state of the glass transition and more recently Chow[22] derived a relationship based on equilibrium thermodynamics which has the utility of being able to predict the depression of T_g of a polymer by a diluent without prior knowledge of the T_g of the pure diluent. The predictive expression applied in these studies has been deduced both by application[16] of the conformational entropy approach[23] to the glass transition and by treating the transition as a purely thermodynamic phase change.[17,18] The latter approach, although the subject of some recent critical discussion,[24,25] treats the glass transition as a second-order transition in the Ehrenfest sense and gives as one convenient form the expression

$$T_{g_{12}} = \frac{x_1 \Delta C_{p_1} T_{g_1} + x_2 \Delta C_{p_2} T_{g_2}}{x_1 \Delta C_{p_1} + x_2 \Delta C_{p_2}} \tag{1}$$

In this equation, 1 and 2 refer to polymer and diluent respectively, x refers to

the mass or mole fraction, T_g is the pure component glass transition temperature, and ΔC_p is the incremental change in heat capacity at T_g.

A limitation of this treatment to polymer-diluent systems in general is the unavailability of values of ΔC_{p_2} for the diluent. This drawback has been noted by other workers;[14] however, in the case of water acting as a diluent, ΔC_{p_2} and T_{g_2} are readily available in the literature.[26, 27]

EXPERIMENTAL

Materials

A series of materials were chosen to represent an amorphous polyamide in a state of increasing compositional and morphological complexity. The first of these, Trogamid T (Dynamit-Nobel), is a wholly amorphous aromatic polyamide formed from the condensation of dimethylphenylene esters and a trimethyl-substituted hexanediamine. The remaining two materials, Bexloy AP C-803 and Bexloy AP C-712 (DuPont), are also composed of an amorphous aromatic polyamide but one of different chemical constitution from that of Trogamid T. These materials also contain a dispersed phase consisting of a rubber impact modifier and the latter also contains an additional component in the form of a dispersed phase of Nylon 12. The compositional and morphological characteristics of all materials were confirmed by calorimetric, spectroscopic, and x-ray techniques, and a summary description is given in Table I. To assist the characterization of the blend containing the Nylon 12 additive, Rilsan AESNO (Nylon 12) was chosen for parallel moisture sorption and calorimetric studies.

Procedures

The materials mentioned above were compression molded into films approximately 1.0 mm in thickness at a temperature of 250°C. These sections were then dried under vacuum for a period of 36–48 h in the presence of phosphorus pentoxide in an Abderhalden-type drying apparatus using refluxing xylene (bp $\simeq$ 140°C) as the heating medium. Dried samples were stored over anhydrous calcium chloride.

TABLE I
Materials and Associated Thermal Properties

| Material | Description | Glass transition temperature | | Incremental change in heat capacity, ΔC_{p_1} |
		Onset (Tg_1) K (°C)[a]	Midpoint K (°C)[a]	J g^1 K^{-1} [a]
Trogamid T	100% Amorphous polyamide	425 (152)	430 (157)	0.39
Amorphous Nylon blend	80% Amorphous polyamide, 20% Impact modifier.	435 (162)	442 (169)	0.39
Amorphous Nylon/ semicrystalline Nylon Blend	60.8% Amorphous polyamide, 20% Impact modifier, 19.2% Nylon 12.	435 (162)	442 (169)	0.39

[a] Measured thermal properties of the amorphous polyamide component.

All T_g determinations, in both dry and moisture-plasticized samples, were performed using a DuPont 1090 Thermal Analyzer equipped with a differential scanning calorimeter (DSC) cell. A heating rate of 20°C/min was employed throughout and all samples were sealed in large volume stainless steel capsules[28] to ensure minimal diluent loss during thermal analysis. Whenever possible both the onset and midpoint of the transition were recorded. The onset T_g is defined here in the usual manner as the point of intersection of the extrapolated base line leading into the transition and a line drawn through the point of inflection of the heat capacity change associated with T_g. The midpoint T_g is defined as the temperature at which half the heat capacity change is reached with respect to the extrapolated base lines before and after the transition.

The incremental change in heat capacity at $T_g(\Delta C_{p_1})$, was determined using a Perkin Elmer DSC Model IV equipped with a thermal analysis data station with sapphire as the specific heat standard. Values of T_{g_1} and ΔC_{p_1} are given in Table I. Dynamic mechanical thermal analysis (DMTA) was performed using a Polymer Laboratories DMTA at a fixed frequency of 10 Hz and a heating rate of 3°C/min.

Moisture imbibition was performed in a manner similar to that described previously.[13] Samples of dry polymer and a small glass ampoule containing a known quantity of water (5–40 mg) were placed in separate segments of a T-shaped glass tube closed at two ends. The whole system was evacuated and flame sealed after which the ampoule was broken by shaking. The assembly was then placed in an oven at 75°C for a period of 36–48 h after which time the polymer samples were removed. In this way moisture imbibition was always effected with the diluent in the vapor phase and the moisture uptake, although only arbitrarily controlled, could be determined accurately by gravimetric methods. Additional samples of each material were also investigated after being allowed to imbibe deionized water at ambient conditions.

RESULTS AND DISCUSSION

Plasticization Studies

The measurement of the thermal properties of Trogamid T, in either the dry or water-plasticized state, presented few experimental difficulties and representative thermograms are shown in Figure 1(a). Note here, as with 1(b) and 1(c), that the thermograms have not been normalized for sample weight and therefore a direct quantitative comparison of the thermograms is not possible. By plotting both the onset T_g and midpoint T_g as a function of moisture content, as shown in Figure 2 (and subsequently for other materials in Figs. 3 and 4), it is possible to establish the effect, if any, of diluent concentration gradients within the prepared samples. A broadening or stretching out of the temperature interval of the heat capacity change associated with the transition could be considered to be the result of a diluent concentration gradient through the sample. These may be formed as a result of not allowing sufficient time for equilibrium to occur during the imbibition process. Some transition width broadening is present at elevated diluent concentrations [see thermograms in Fig. 1(a)], however, it is unlikely to have been
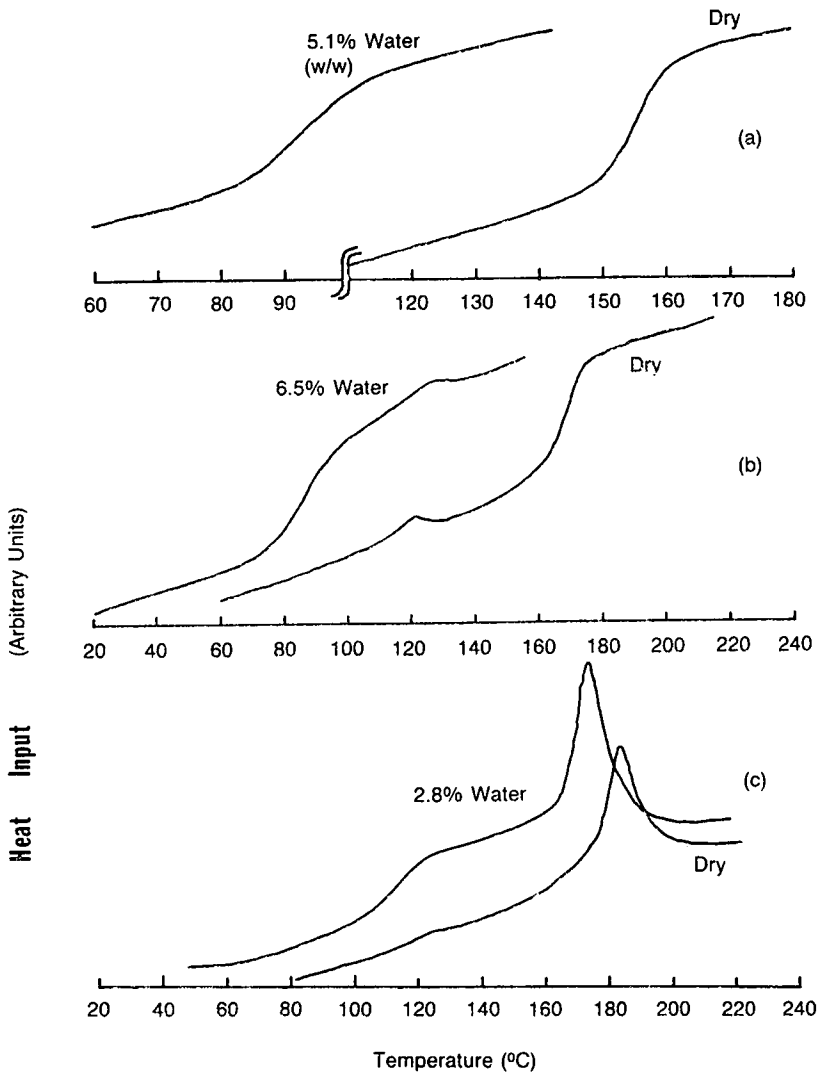
Fig. 1.   Representative thermograms of dry and moisture-plasticized materials: (a) Trogamid T; (b) Amorphous polyamide/rubber blend; (c) amorphous polyamide/Nylon 12/rubber blend.

caused by poor sample preparation. Transition width broadening is also a common feature in miscible polymer–polymer blends, usually in the middle composition range.[29] Also included in Figure 2 are data obtained from saturated equilibrated specimens allowed to imbibe water at ambient conditions, usually over a period of approximately 2 months. Inspection of the data points at $x_2 = 0.05$ demonstrates that there is no significant difference between the results obtained by this method of moisture imbibition and the accelerated method performed at 75°C over two days. Moisture equilibrated samples produced at an elevated temperature, when redried under vacuum, exhibited no significant changes in original thermal properties and therefore it is possible to exclude potential contributory effects of chemical reactions between diluent and polymer.
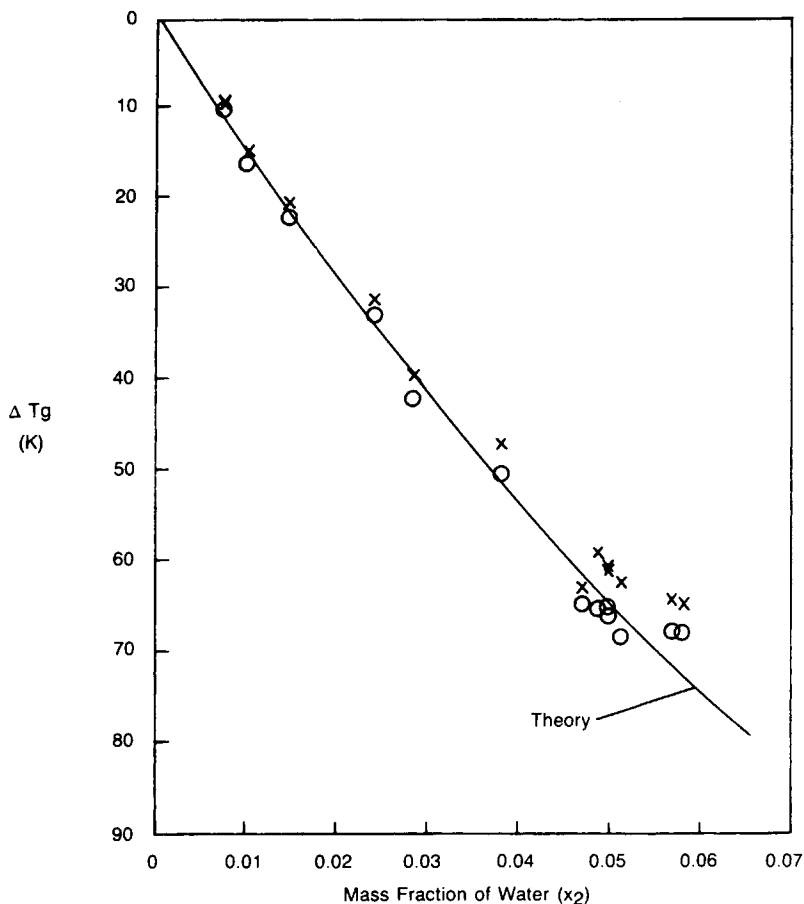
Fig. 2. Depression of glass transition temperature of Trogamid T as a function of water content: (○) onset T_g; (×) midpoint T_g.

Included in Figure 2 is the predicted depression of T_g calculated using Eq. (1), and as can be seen, agreement with experimental results is excellent. In these and subsequent calculations, the results of which are shown in Figures 3 and 4, the onset T_g was used as the value for T_{g_1}. Equation (1) is relatively insensitive to small changes of T_{g_1} and we can view the predictive plot to be representative of both the depressed onset and midpoint T_g. For example, in the case of Trogamid T containing a diluent mass fraction of 0.05, substituting the midpoint T_g for T_{g_1} shifts the theoretically depressed T_g by only 1.2°C. Calculations were performed using $\Delta C_{p_1} = 1.94$ J/g K and $T_{g_2} = 134$ K.[26,27] Previous work of a similar nature has shown the value of T_{g_2} used here to be sensible and consistently reliable.[30,31]

The analysis of the amorphous polyamide blend containing only the rubber additive is again relatively straightforward. Representative thermograms of dry and water plasticized samples of this blend are shown in Figure 1(b). The slight endotherm in the dry sample at approximately 120°C is attributed to melting of crystallites in the olefonic-based impact modifier. The analysis of this blend requires not only the measured value of ΔC_{p_1} to be corrected by a
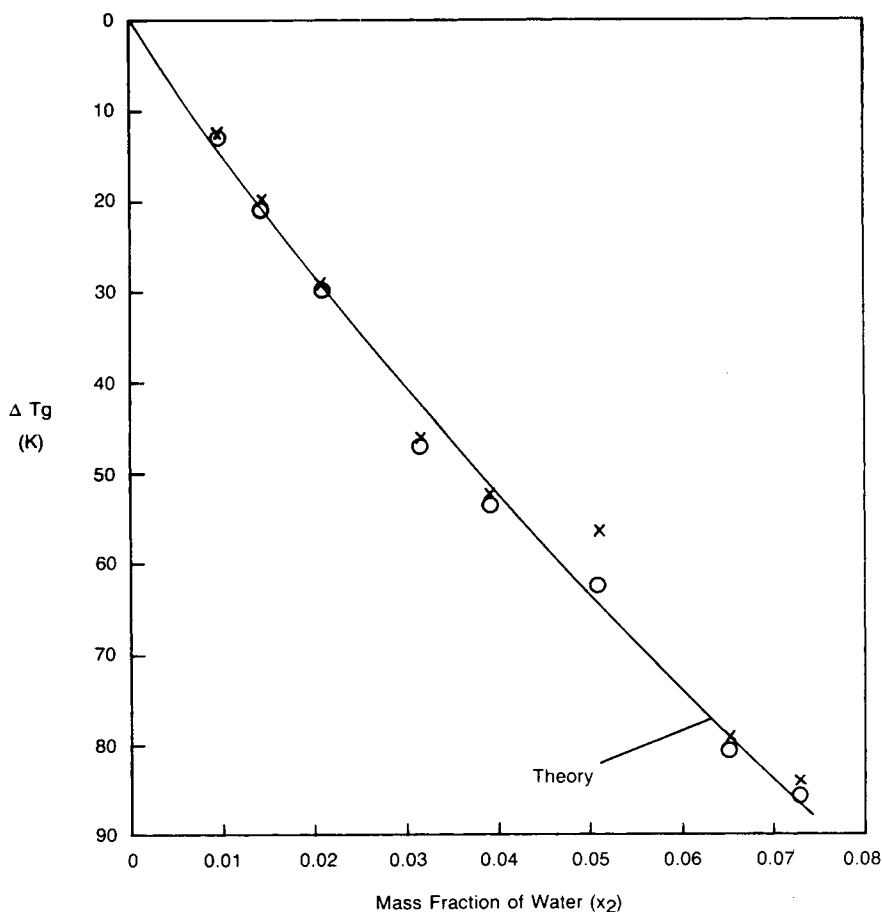
Fig. 3.   Depression of glass transition temperature of the amorphous polyamide component of the amorphous polyamide/rubber blend as a function of respective water content; (○) onset T_g; (×) midpoint T_g.

factor representative of the loading of the rubber additive, as mentioned previously, but also the true moisture content of the amorphous polyamide component has to be corrected using the same factor. The correct water content of the amorphous polyamide phase has been computed by assuming that no water resides in the rubber phase. Results from DMTA of a dry blend indicated one peak value for the loss modulus at −42°C which is attributed to the T_g of the rubber modifier phase. Similar analysis of a moisture-plasticized sample produced an identical result. Therefore, it is possible to conclude that the assumption described above is reasonably valid. Even if this phase did assume a small quantity of moisture (< 1%), its effect on the calculated moisture content of the polyamide phase would be minimal since it only forms 20% by weight of the total. The experimental data presented in Figure 3 have been expressed in terms of the calculated moisture content, that is, the true moisture content, of the polyamide. As can be seen, excellent agreement between theory and experiment has also been obtained.
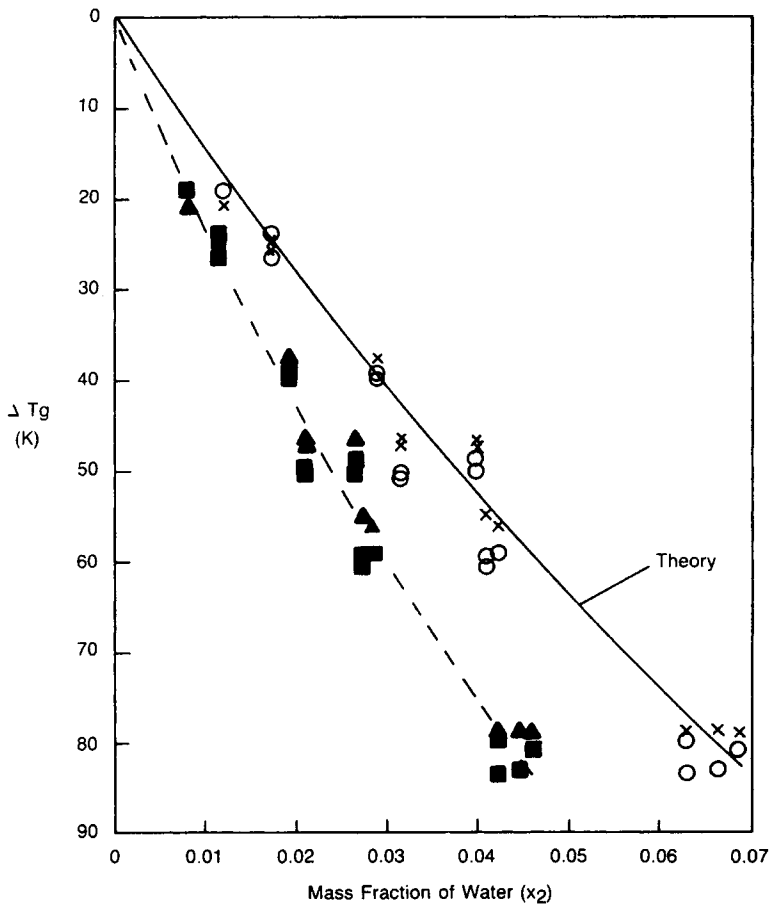
Fig. 4. Depression of glass transition temperature of the amorphous polyamide component of the amorphous polyamide/Nylon 12/rubber blend as a function of water content; expressed both in terms of total material mass (■, onset T_g; ▲, midpoint T_g) and respective mass of amorphous polyamide (○, onset T_g; ×, midpoint T_g).

The same experimental procedures and safeguards were followed as those described previously for Trogamid T. The experimental points at approximately 0.051 mass fraction of diluent (5.1% w/w) in Figure 3 illustrate the effect of a nonequilibrated plasticized sample produced by soaking in deionized water under ambient conditions. The enhanced broadening of the transition, of the nature described previously, can be attributed in this case to a diluent concentration gradient within the sample. A similarly prepared sample saturated to a uniform water content ($x_2 \simeq 0.073$) did not show this large transition width.

The study and analysis of the amorphous polyamide/Nylon 12 blend presented an additional complexity attributable to the incorporation of Nylon 12. As in the case of the blend described previously, the presence of an approximate 20% by weight of the impact modifier was noted during calorimetric analysis by a small endotherm at approximately 120°C [see Fig. 1(c)]. This component was again treated as a phase-separated hydrophobic compo-

nent with an insignificant moisture regain. The major difficulty associated with the analysis of this blend was manifested by the presence of a large melting endotherm superimposed on the heat capacity change associated with a glass to rubber transition of the amorphous polyamide. The peak maximum of this endotherm 183.0°C [see Fig. 1(c)] is in good agreement with literature values for the melting point of Nylon 12.[32] In addition the estimated heat of fusion of this crystalline constituent, (40–50 J/g, based on the estimated loading of 19.2% by weight), is in good agreement with that obtained here for the Nylon 12 standard, (ΔH_f = 45–50 J/g, mp = 186°C). Although a heating thermogram of this blend did not allow any of the characteristic transition parameters of the amorphous polyamide constituent to be determined, a cooling thermogram, simplified by the slight supercooling of the crystalline component, clearly indicated a rubber to glass transition from which the estimated midpoint was found to coincide with that obtained from a cooling thermogram of the amorphous polyamide/rubber blend. An important corollary of these observations is that the Nylon 12 appears to be immiscible with the amorphous polyamide and therefore forms a distinct separate phase within the blend. Since both these polyamides are hydrophilic, any moisture absorbed by the blend will be distributed unevenly between the amorphous polyamide and Nylon 12 phases.

Experimental studies of water-plasticized samples of this blend indicated a depressed glass transition of the amorphous polyamide phase and a slightly depressed T_m of the Nylon 12 component. As a result of the disproportionate decrease of the T_g of the amorphous polyamide, relative to the reduction of T_m of Nylon 12 in the blend, the plasticized T_g could be determined unambiguously. The T_g of the Nylon 12 component could not be detected by calorimetry either in the blend or in a rapidly cooled sample of pure Nylon 12 and therefore was not subjected to investigation. However, it was possible to detect a T_g for Nylon 12 in the blend using DMTA. The depression of T_g of the amorphous polyamide expressed as a function of the water content of the blend as a whole is presented in Figure 4. Also shown here is the predicted depression of T_g for the amorphous polyamide, similar to that given in Figure 3, and not surprisingly the agreement between theory and experiment is poor.

In order to express the experimental data as a function of the true moisture content of the amorphous polyamide phase, the following approach was adopted. Parallel moisture sorption studies of the Nylon 12 were performed that allowed the construction of a calibration curve as shown in Figure 5. If it is assumed that, at the same partial pressure of diluent, the Nylon 12 phase of the blend assumes the same moisture content as the pure Nylon 12, then from a knowledge of the total moisture absorbed by a sample of the blend and the respective loading of Nylon 12, it is possible to calculate the moisture content of both phases. Experimental studies on a phase-separated blend of two hydrophilic polymers, although different from those under investigation here, have shown that moisture sorption by a minor component in the blend is not significantly different from that measured in the pure state.[33]

The experimental data expressed as a function of the computed true moisture content of the amorphous polyamide phase are also shown in Figure 4 and, as can be seen, agreement between theory and experiment has been improved substantially. The linear relationship obtained in Figure 5 is only
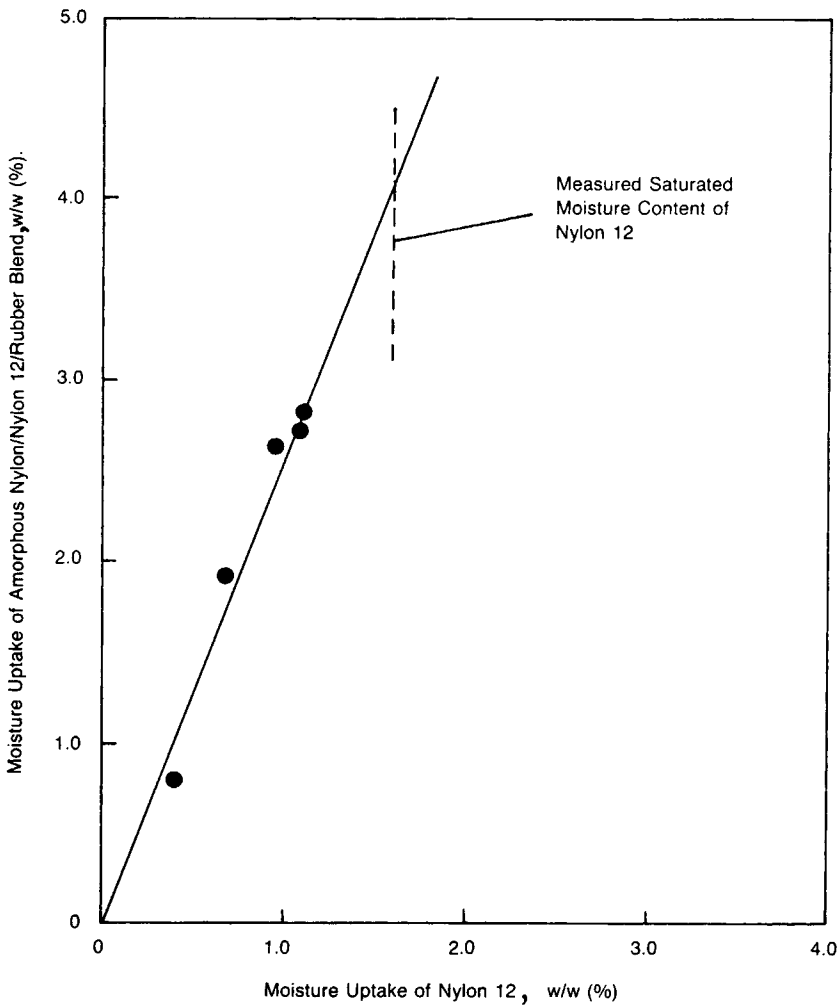
Fig. 5. Moisture absorption of the amorphous polyamide/Nylon 12/rubber blend versus the moisture absorption of 100% Nylon 12 under identical conditions.

applicable up to the saturated moisture regain of Nylon 12, measured in these studies as approximately 1.6% by weight. Therefore samples of the blend allowed to imbibe moisture at a level of 4.1% by weight and above contain a saturated Nylon 12 phase with the excess moisture residing in the amorphous polyamide. It should be remembered that since all moisture content measurements are made at ambient conditions, an important aspect of the treatment of this blend and the experimental data relies implicitly on the phase stability of the polymer-polymer-solvent ternary system up to the elevated temperatures necessary to conduct thermal analysis. As will be described later, there is experimental information to support this assumption. It has also been assumed that the respective water content of the two phases remains constant during thermal analysis. This requirement, necessary to conduct the analysis, is more difficult to verify.

Melting Point Depression of Nylon 12 by Water

To augment the interpretation of the moisture sorption behavior of the amorphous polyamide/Nylon 12 blend, the melting point depression of the Nylon 12 component was determined. The physical basis for the depression of the melting point of a semicrystalline polymer by a diluent is well understood and the theoretical description of this phenomenon[34] has been shown to be very successful in predicting observed behavior.[35] Moreover, the theory has proved so successful that it forms part of an accepted procedure for the evaluation of the enthalpy of fusion of the completely crystalline form of a polymer, namely ΔH_u of 100% crystalline polymer. The expression commonly used is presented in the usual form as:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{RV_u}{\Delta H_u V_1}\left[\nu_1 - \frac{BV_1}{RT_m}\nu_1^2\right] \tag{2}$$

where T_m and T_m^0 are the equilibrium melting points of diluted polymer and pure polymer, respectively, V_1 and V_u are the molar volumes of the diluent and polymer chain repeat unit, respectively; ΔH_u is the molar enthalpy of fusion of the repeat unit of the polymer, ν_1 is the volume fraction of diluent expressed in terms of total polymer volume and B is a parameter that characterizes the interaction energy density of the polymer-solvent pair.

Usually an important criterion for the application of the theory is that melting points should be measured at equilibrium and therefore experiments normally demand a very slow heating rate (1°C/day) for their evaluation. This in turn imposes experimental limitations particularly with regard to polyamide/water systems where diluent volatility and the possibility of chemical reactions at high temperature would compromise experimental results. Nevertheless some semicrystalline polyamides diluted with high boiling point liquids have been investigated by this rigorous procedure.[36] The determination of T_m using a high heating rate of 20°C/min, although used here to facilitate T_g measurements, is not recommended for the reason already mentioned. However, several successful studies of the evaluation of the depression of melting point of a semicrystalline polymer by diluents have been performed using calorimetry at faster heating rates than those usually employed.[37]

In general, the Nylon 12 component of the blend experienced an approximate 13°C depression of T_m for a calculated water content of approximately 1.6% of weight. It was not possible to verify this observation by reference to the literature. However, studies on acrylic polymer/water systems suggest that this result is of the expected order of magnitude.[38,39] In all cases the endothermic peak maximum was taken as the measure of T_m and the results are presented in Table II. By again assuming that the phase behavior of the polymer-polymer-water ternary system remains stable up to the T_m of Nylon 12, the volume fraction of water at 185°C has been calculated as shown in Table II. Parallel melting point depression studies of the pure Nylon 12 were compromised by inconsistent melting behavior probably related to the evolution of moisture during thermal analysis. The fact that this was not a problem in the blend can be attributed to the ability of the amorphous polyamide matrix to act as a barrier to rapid moisture loss.

Melting Point Depression of Nylon 12 in the Amorphous Nylon/Nylon 12/Rubber Blend

Mass fraction of water in blend	Mass fraction of water in Nylon 12 phase m_f	Volume fraction of water in Nylon 12 phase[a] $\nu_1{}^{c}$	Melting point, T_m K (°C)
0	0	0	456.2 (183.0)[b]
0.0421	0.0165	0.0177	443.6 (170.4)
0.0421	0.0165	0.0177	442.6 (169.4)
0.0209	0.00825	0.0089	449.7 (176.5)
0.0209	0.00825	0.0089	448.5 (175.3)
0.0114	0.0045	0.0048	449.9 (176.7)
0.0114	0.0045	0.0048	451.0 (177.8)
0.0272	0.0107	0.0115	444.2 (171.0)
0.0079	0.0032	0.0034	452.8 (179.6)
0.0191	0.0077	0.0083	448.5 (175.3)
0.0191	0.0077	0.0083	448.4 (175.2)
0.0446	0.0175	0.0188	440.7 (167.5)
0.0460	0.0180	0.0193	443.2 (170.0)

[a] Calculated assuming zero volume of mixing at 185°C using $\rho_{H_2O} = 0.887$ g cm^3 (Ref. 40) and $\rho_{Nylon\ 12} = 0.952$ g cm^3 (Ref. 41).

[b] T_m^0 [see Eq. (2)].

[c] ν_1 has been calculated using the following expression: $\nu_1 = \dfrac{\dfrac{m_f}{\rho_{H_2O}}}{\dfrac{m_f}{\rho_{H_2O}} + \dfrac{(1 - m_f)}{\rho_{Nylon\ 12}}}$.

For very concentrated polymer solutions (i.e., low diluent concentrations), Flory's approximation of Eq. (2)[34] has been shown to give satisfactory agreement with experimental data[42] and it has also been applied here to simplify the analysis. The expression is given as:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R V_u}{\Delta H_u V_1}(\nu_1) \tag{3}$$

A plot of $1/T_m - 1/T_m^0$ against ν_1 yields a linear relationship as shown in Figure 6. As already stated, the ambient saturated equilibrium moisture content of Nylon 12 is approximately 1.6% by weight, which is representative of a volume fraction of $\nu_1 = 0.017$. The slightly erroneous position of the group of data points above this value suggests that this limiting moisture content is also appropriate to higher temperatures.

From the slope of $1/T_m - 1/T_m^0$ against ν_1, and using values of V_u and V_1 of 207.2 cm^3/mol and 20.3 cm^3/mol, respectively, the value of ΔH_u was calculated to be approximately 100 J/g, (4.6 K cal/mol). Literature values obtained from copolymerization (225 J/g,[43] 63 J/g[44]) and calorimetric (134 J/g[44]) methods differ quite markedly. It is probable, though, that a value closer to 200 J/g is the more likely to be true. This can be justified by comparing the more useful quantity ΔS_u/bond/cal/K, the entropy change associated with melting. The value of 0.73, obtained using $\Delta H_u = 100$ J/g, is
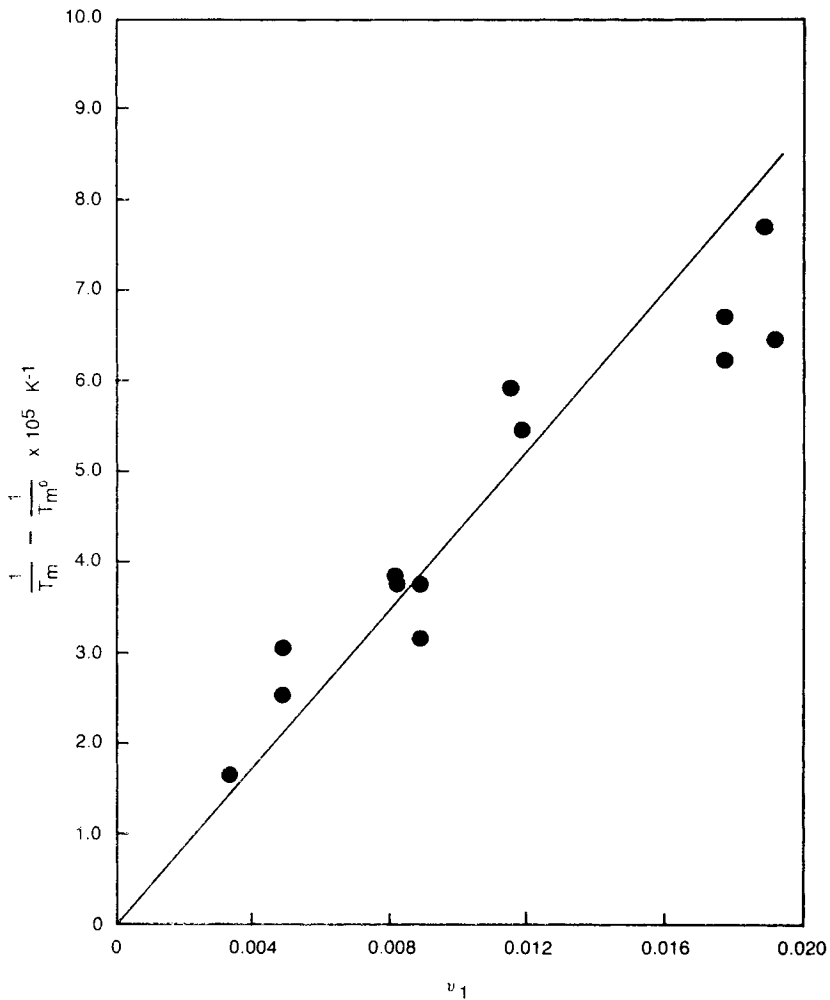
Fig. 6. Depression of melting point of the Nylon 12 component of the amorphous polyamide/Nylon 12/rubber blend as a function of volume fraction of water (v_1).

approximately one half that obtained for other semicrystalline polyamides of similar chemical composition,[45] and therefore since ΔH_u is approximately proportional to ΔS_u for the semicrystalline polyamides it is probable that the value obtained here for ΔH_u is also in error by a factor of 0.5. Reasons for this discrepancy may lie in several areas, but it is perhaps worth emphasizing that good agreement could be obtained if the volume fraction of diluent had been underestimated. An underestimate of the quantity of diluent necessary to produce the observed depression of T_m would not significantly affect the results or arguments presented in the preceding section for the plasticization of the amorphous polyamide. The Nylon 12 is only a minor component and changes in the distribution of water between this phase and the amorphous polyamide phase has a small influence on the overall water content of the latter. If the extreme position is assumed, where we suspend the requirement that the Nylon 12 can only absorb a maximum water content of 1.60% by

weight and assume a systematic error in the estimation of ν_1, then it is possible to calculate the volume fraction of diluent necessary to give the depression of T_m measured with a value of $\Delta H_u = 200$ J/g. For example, under these conditions the blend with a total moisture content of 4.21% by weight would actually be representative of a moisture content of 3.01% and 5.90% in the Nylon 12 and amorphous polyamide components, respectively. These results may be compared with previous calculations which had given respective values of 1.60% and 6.30%. Thus a relatively large change in the moisture content of the Nylon 12 phase has only a small influence on the moisture content of the amorphous polyamide. The foregoing questions the important assumption that the two polyamides are completely immiscible. Partial miscibility, although in this case difficult to detect, may not substantially affect the explanation of plasticization studies, and would be consistent with an underestimate of the moisture content in the Nylon 12 phase.

It is unlikely, however, that the failure of precise agreement between theory and experiment in the analysis of the depression of T_m by water is totally attributable to error in the estimation of ν_1. Nevertheless the level of agreement obtained does substantiate the approach adopted in both the interpretation of the blend phase behavior and in its interactions with water.

Morphology and Plasticization

The preceding section has alluded to the difficulties associated with obtaining the correct interpretation of morphology and how it influences accessibility to moisture in a complex hydrophilic material. Within this context there are several features of the results presented here worthy of special emphasis and discussion.

As a general observation, the amorphous polyamides investigated here undergo a 15°C depression of T_g by the addition of 1% by weight of water and are capable ultimately of absorbing up to 6–7% by weight water leading to a substantial overall decrease of T_g of approximately 70–85°C. These results are consistent with previous measurements on other hydrophilic polymers,[10,30] and the relatively large reduction of T_g is clearly consistent with, and supportive of, the theory applied here.

By considering the moisture sorption potential of polyamides in terms of the relative concentration of amide functionalities, it is possible, as a first-order approximation, to illustrate further the influence of morphology on Nylon–water interactions. The amorphous polyamides studied here have a low concentration of amide functionalities compared to Nylon 6, yet they absorb slightly more water than Nylon 6 when based on the total mass of polymer. The crucial difference, however, is that all of the amorphous polyamide is accessible to the water molecules whereas in Nylon 6 only the noncrystalline regions are accessible.

There is no reason to believe that, with respect to plasticization by water, amorphous Nylon 6 molecules should behave any differently than those of the amorphous aromatic polyamides. Moreover, by using a value of $\Delta C_p = 0.83$ J/gK for amorphous Nylon 6,[46] the situation with regard to the moisture induced plasticization of the semicrystalline polyamides becomes more clear. This relatively large value of ΔC_p has been determined by a rigorous extrapo-

lation procedure and because of the difficulties associated with a direct measurement (cf., $\Delta C_p = 0.25$ J/gK[19]) can be considered to be more representative of amorphous Nylon 6. In addition, work currently in progress in this laboratory involving measurement of the composition-dependent T_g of miscible blends containing Nylon 6 has also indicated this to be a realistic value. The substitution of this value of ΔC_p into Eq. (1) provides for only a small reduction of T_g for amorphous Nylon 6; of the order of 4–5°C for 1% by weight of water. Paradoxically this result is at variance with that normally encountered in the literature where a reduction of between 15°C and 30°C for 1% by weight of water in Nylon 6 fairly typical. In view of the preceding discussion, this apparent discrepancy can be attributed to the ability of morphology to mask the correct interpretation of the plasticizing efficiency of water in this material by underestimating the local moisture concentration of the amorphous regions. The true response of this material could be resolved by identifying the amorphous regions, their absolute quantity and their local moisture content when exposed to water.

CONCLUSIONS

Amorphous polyamides in pure and blended form exhibit a monotonic depression of the glass transition temperature as a function of water content. By careful consideration of composition and morphology, and their concomitant influence on measured thermal properties and distribution of plasticizer within these materials, it has been possible to obtain a good correlation of experimental results with a theoretical predictive treatment of the composition-dependent T_g of polymer-diluent binary systems. The precise ability of the theory to account for hydrophilic polymer–water systems as well as nonpolar polymer–diluent systems lends further credence to the straightforward plasticizing action of water in polar polymers.

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