

Effect of Water on the Glass Transition Temperature of Hydrophilic Polyurethanes

NATHANIEL S. SCHNEIDER,^{1,*} JOYCE L. ILLINGER,² and FRANK E. KARASZ³

¹Geo-Centers, Inc., 7 Wells Avenue, Newton, Massachusetts 02159; ²Army Materials Technology Laboratory, Polymer Research Branch, SLCMT-EMP, Watertown, Massachusetts 02172; ³Polymer Science and Engineering Department, University of Massachusetts Amherst, Massachusetts 01003

SYNOPSIS

The depression of the glass transition temperature by water was studied in a set of polyurethanes in which the soft segment consisted of polyethylene oxide (sample I) or a block copolymer of poly(propylene oxide) terminated with poly(ethylene oxide) in various proportions (sample set II). DSC measurements were made at two added water contents for each type of sample and at various temperatures. The T_g reduction appeared to be governed solely by the nonfreezing bound water and was much larger in sample I than in samples of set II. The more limited effect on the T_g of set II samples is attributed to restricted mobility arising from coupling of the short terminal poly(ethylene oxide) to rigid hard-segment units. Therefore, the data for sample I are preferred as a test of the predictive relations for the T_g depression. On this basis, it appears that the simple Fox mixing equation is more reliable than is the available free volume approach, which required unrealistically high values of the thermal expansion coefficient for water to fit the data for sample I.

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INTRODUCTION

There is considerable interest in hydrophilic polyurethanes as fabric coatings for certain types of clothing for which high moisture transmission rates are an advantage in improving comfort. The level of interest is reflected in the numerous publications of a practical nature concerned with assessing the performance of these materials.¹⁻³ More fundamental studies of water interactions with hydrophilic polyurethanes have received only limited attention. The properties of a series of polyurethanes in which water solubility was controlled by varying the proportion of poly(propylene oxide) and poly(ethylene oxide) used to form the mixed soft segment was reported by Tobolsky and co-workers.⁴ The study included measurements of the water uptake and the water and salt permeabilities determined by osmosis. Illinger studied a related series of polyurethanes in which the soft segment was either poly(ethylene

oxide) or a block copolymer with a central propylene oxide segment terminated by poly(ethylene oxide) with various proportions of the two segments.⁵ Her results were reported in two papers.^{6,7} The first presented DSC data that defined the amount of nonfreezing bound water as a function of the soft-segment variation and of sample equilibration temperature. A free-volume expression for the glass transition lowering as a function of the bound water content was also tested. The calculated values provided a reasonable estimate of the results for the polymers containing block copolymer soft segments, but seriously underestimated the glass transition lowering in the pure poly(ethylene oxide) containing polyurethane. The second paper was concerned with water-vapor transport measurements on these polymers.

Recently, the data obtained by Illinger have been reexamined in order to explain the unusual temperature dependence of the saturation water content in the samples with block copolymer poly(ethylene oxide)/poly(propylene oxide) soft segments.⁸ It was concluded that the two components of the block copolymer soft segment were incompatible and that

* To whom correspondence should be addressed.

the behavior reflected an increase in phase compatibility with increasing temperature. The present paper continues the reexamination of the data from Illinger's studies, in this case concerning the relation between the water content and the glass transition lowering. The current analysis is constrained by some problems in the original data. Nonetheless, it will be possible to reach some conclusions about the applicability of expressions for the depression of the glass transition temperature and some of the controlling factors.

EXPERIMENTAL

Polyurethane samples were formed from diphenyl methane diisocyanate (MDI), butanediol (BD), and a macroglycol (PE) in several mole ratios. The soft segment consisted of pure poly(ethylene oxide), molecular weight 1450 (Union Carbide) or of one of three block copolymers of poly(propylene oxide)–poly(ethylene oxide), molecular weight 2000 (Wyandotte Corp.), each with a different ratio of the two components. The notation 5PE33 designates a sample with 50% by weight of poly(ethylene oxide) in the soft segment and 33% MDI in the hard segment, which corresponds to a 4/3/1 mol ratio of MDI, BD, and PE. This paper focuses mainly on the results for the samples with the pure poly(ethylene oxide) soft segment, 10PE33, and the above-mentioned 5PE33. Details of the synthesis⁷ sample composition and other properties⁸ have been reported earlier.

DSC studies were made with a Perkin-Elmer DSC-2 that had a subambient accessory cooled with liquid nitrogen and purged with helium. Samples were prepared from films cast from *N,N*-dimethylformamide (DMF) solution and dried under vacuum for 48 h at 50°C. The polymer discs of known dry weight were equilibrated with water, transferred to large-diameter, custom-fashioned, gold-foil pans, and the excess water was allowed to evaporate on the microbalance to the desired water content before hermetically sealing the pans. Samples were equilibrated at 10° intervals from 273 to 323 K (T_{eq}), quenched at a setting of 320° per minute to 150 K, then scanned at 20°/min to T_{eq} .

RESULTS AND DISCUSSION

The set of DSC traces for 10PE33 equilibrated at 323 K, with various amounts of added water, appears in Figure 1. These results illustrate the change in

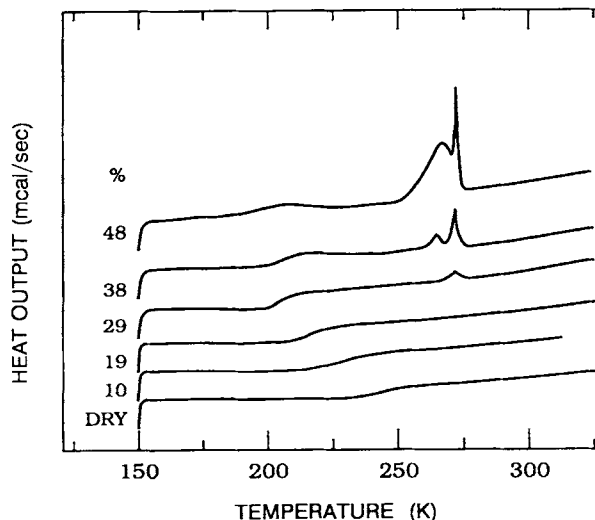


Figure 1 DSC scans of 10PE33 equilibrated at 273 with various amounts of added water. The added water is shown as grams water per 100 grams of polymer. By permission from Ref. 5.

the state of water with increasing added water, from nonfreezing bound water at low amounts of added water to the onset of a broad endotherm (representing bound freezing water) and, finally, a sharp peak at 273 K, which indicates the melting of free dissolved water below the saturation concentration of 58%. It is apparent that the glass transition temperature decreases continuously with the amount of added water. It is this aspect of the data that is the focus of the present paper.

Tables in Ref. 5 record the amount of bound nonfreezing water obtained as the difference in the amount of water included in the endotherms and the amount of added water. The values were calculated using the melting enthalpy of bulk water, 79.8 cal/g. No data were provided on the separate values of the bound freezing water and the free water, but it is possible to reconstruct values for the bound freezing water. The results on the state of water and the depression of the glass transition temperature are summarized in Table I for the set of polyurethane samples at the indicated amounts of added water and for the series of equilibration temperatures. The first column of data for each sample lists the amounts of nonfreezing bound water, in units of grams of water per 100 grams of PEO. The second column of data is the amount of freezing bound water. At the three lower equilibration temperatures, where the amount of added water is below saturation, the freezing bound water was estimated as the difference between the amount of nonfreezing bound water from tables in Ref. 5 and the amount

Table I Effect of Changes in the Amount of Bound Water on ΔT_g , the Depression of T_g

Sample	Added Water ^a	Equilibrium Temp (K)	Bound Water (g Water/100 g PEO)		ΔT_g
			Nonfreezing	Freezing	
10PE33	124%	273	62	62	49
		283	52	72	46
		293	54	63	48
		303	57	50	50
		313	50	44	40
		323	19	63	24 ^b
5PE28	157%	273	120	37	31
		283	116	41	31
		293	42	115	9 ^b
		303	102	21	21
		313	85	0	26
		323	28	12	7 ^b
5PE33	111%	273	105	6	24
		283	98	13	25
		293	66	45	19 ^b
		303	71	13	18
		313	19	38	2 ^b
		323	16	15	1
5PE40	79%	273	79	0	27
		283	79	0	27
		293	68	11	24
		303	23	38	8 ^b
		313	37	6	12
		323	22	5	6 ^b

^a Added water in grams water per 100 g PEO.^b Values of ΔT_g that illustrate the correlation with sudden changes in the amount of nonfreezing bound water.

of added water. The saturation water content decreases with increasing temperature with the result that the added water exceeds the saturation content at 303 K and the two higher equilibration temperatures in all cases. For these conditions, the amount of freezing bound water was calculated as the difference between the nonfreezing bound water and the saturation concentration. It is possible to have water that melts at 273 K, even at an added water content that is below saturation. This water represents free water that is dissolved in the polymer and has a mobility much lower than does bulk water.⁹ The amount of freezing bound water will be overestimated to the extent that this has occurred in these samples. However, it will develop that the analysis of interest for the glass transition behavior is not dependent on accurate values of the freezing bound water.

The first question to be addressed is whether the glass transition temperature is dependent on the total amount of dissolved water or only on the amount

of nonfreezing bound water. The T_g for 10PE33 appears to be essentially independent of temperature. The T_g for the other samples appears to change in a marked way only at 303 K and above. The change at this temperature is probably related to changes in the phase compatibility of the two components of the soft segment, which also influences the saturation water content. Some insight on the relative importance of the state of water is indicated by the T_g results shown in Table I that represent instances of a marked decrease in T_g relative to neighboring values. It will be noted that in almost all these cases there is a marked decrease in the amount of nonfreezing bound water and a corresponding increase in the amount of freezing bound water. This observation suggests that the controlling factor is the amount of nonfreezing bound water rather than the total amount of dissolved water. This conclusion is consistent with the assumption that Illinger made in analyzing her results.⁶

One method of calculating values of the glass

transition temperature involves the use of the Fox equation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

where w_1 represents the weight fraction of nonfreezing bound water in the poly(ethylene oxide) component of the soft segment, w_2 represents the weight fraction of poly(ethylene oxide) in the water poly(ethylene oxide) mixture, T_{g1} denotes an appropriate value for the glass transition temperature of water, and T_{g2} is the glass transition temperature of poly(ethylene oxide) in the dry polymer. Extrapolated values of various salt solutions and direct measurements on quenched amorphous water have provided a value of 137 K for T_{g1} . However, a later study,¹⁰ utilizing DSC measurements, concluded that no glass transition is observed for water at that temperature and that the transition occurs at much higher temperature but is obscured by the rapid crystallization of the quenched glass in the range of 150–162 K. For the purpose of the present calculations, 165 K has been used for the alternative T_{g1} .

Selected results, which illustrate the effect of using the two values of T_{g1} , appear in Table II. From these results, it is apparent that the value for T_{g1}

has a marked effect on the calculated values of T_g . Use of $T_{g1} = 137$ K provides a close fit to the data for 10PE33 with 124% (grams of water per 100 g PEO) added water, but a poor fit to the data for all other samples, exemplified by 5PE33. The calculations with $T_{g1} = 165$ K provide a close fit to the data for 10PE33 with 78% added water. The fit to the data for the other samples is somewhat improved over the previous calculations, as indicated again by results for 5PE33, but is still poor.

It is also possible to carry out calculations of the depression of T_g in terms of free-volume concepts, using the following expression derived by Bueche and summarized by Meares¹¹ who gave examples of the application:

$$T_g = \frac{v_2 T_{g2}(a_l - a_g) + v_1 T_{g1} a_1}{v_2(a_l - a_g) + v_1 a_1}$$

Here T_g is the depressed glass transition temperature; T_{g2} and T_{g1} are the glass transition temperatures of polymer and diluent, respectively; v_2 and v_1 are the corresponding volume fractions; $(a_l - a_g)$ is the difference in expansion coefficients of polymer liquid and glass; and a_1 is the thermal expansion coefficient of the diluent. Because the thermal ex-

Table II Calculated and Experimental Values for T_g Using the Fox Mixing Relation

Sample (Added Water) ^a	Equilibrium Temp (K)	Bound Water g/g PEO	Exp T_g^b (K)	Calculated Values		
				T_g for 137 K	ΔT_g for 137 K	ΔT_g for 165 K
5PE 33 (111%)	273	0.510	210.3	171.4	38.9	18.1
	283	0.492	207.5	172.9	34.6	14.2
	293	0.294	214.1	182.2	30.8	13.0
	303	0.412	214.1	190.5	33.6	15.3
	313	0.160	230.5	208.9	21.6	12.6
	323	0.138	231.8	211.7	20.1	12.1
10PE33 (78%)	273	0.355	204.6	190.3	14.3	-3
	283	0.315	204.5	194.9	9.6	-6.5
	293	0.338	206.0	192.2	13.8	-3.1
	303	0.333	204.1	192.8	11.3	-5.3
	313	0.324	203.9	193.8	10.1	-6.3
	323	0.281	222.0	199.2	22.8	8.0
10PE33 (124%)	273	0.383	193.8	187.1	6.7	-11.5
	283	0.342	196.5	191.7	4.8	-12.2
	293	0.351	194.4	190.7	3.7	-13.6
	303	0.363	191.5	189.3	2.3	-15.3
	313	0.333	194.7	192.8	1.9	-14.7
	323	0.160	208.2	215.6	-7.4	-17.0

In the above, ΔT_g = experimental T_g - calculated T_g .

^a Added water in grams water per 100 g PEO.

^b Experimental T_g .

pansion coefficient of water at the temperature of the polymer glass transition is not known, it is used as a fitting parameter. The results in the first column of data in Table III reproduce some of calculations carried out by Illinger using the following values:

$$a_1 = 2.07 \times 10^{-4}, \quad (a_l - a_g) = 4.8 \times 10^{-4}$$

and $T_g = 137 \text{ K}$

The results are again recorded as the difference between the calculated and measured glass transitions for the three samples chosen to illustrate the trend. The predicted T_g , on average, is about 6° lower than the measured value for the block copolymer sample but more than 15° too high for 10PE33 with 78% water and almost 30° higher than results with 124% water. With the alternative water value, $T_{g1} = 165 \text{ K}$, it is necessary to increase a_1 to 3.0×10^{-4} to match the previous results for 5PE33, as shown in

the next column. There is little improvement in the values for 10PE33, which, however, are still too high. To bring the predicted values for 10PE33 into line with the measured values, it is necessary to increase a_1 to 8×10^{-4} . The results in the last column show that a match is achieved for 10PE33 with 124% water, but the depression of T_g for 5PE33 is seriously overestimated. Furthermore, this value of the thermal expansion coefficient is unrealistically high. The thermal expansion coefficient of water ranges from about 2.6 to 5.0×10^{-4} at temperatures between 30 and 60°C .

It is not clear why the fit with the free-volume relation is far closer for the samples with the block copolymer soft segments. However, a review of the data of Table I shows clearly that the nonfreezing water, compared at equivalent amounts, is far more effective in lowering the glass transition temperature of the sample with the pure poly(ethylene oxide)

Table III Difference between Calculated and Experimental Values of T_g Using the Free-volume Relation

Sample (Added Water) ^a	Equilibrium Temp (K)	ΔT_g		
		T_g^b		
		137 K	165 K	137 K
		a_1^c		
		2.1×10^{-4}	3.0×10^{-4}	8.0×10^{-4}
5PE33 (111%)	273	7.7	4.7	38.5
	283	3.5	0.8	34.2
	293	1.8	0.4	30.4
	303	4.1	2.5	33.3
	313	5.7	5.6	21.3
	323	5.9	5.9	19.8
10PE33 (78%)	273	-17.3	-17.7	12.8
	283	-20.1	-20.3	8.1
	293	-17.1	-17.4	12.2
	303	-19.3	-19.6	9.8
	313	-20.1	-20.3	8.6
	323	-4.9	-4.9	21.4
10PE33 (124%)	273	-26.0	-26.7	5.2
	283	-26.3	-26.6	3.3
	293	-27.8	-28.2	2.1
	303	-29.7	-30.2	0.8
	313	-28.7	-29.0	0.4
	323	-25.8	-25.6	-8.5

In the above, $\Delta T_g = \text{experimental } T_g - \text{calculated } T_g$.

^a Added water in grams water per 100 g PEO.

^b Water T_g .

^c Thermal expansion coefficient of water.

soft segment. Therefore, it cannot be expected that any single approach would be equally successful with both classes of samples. In addition, there is also the difficulty that the T_g depression is somewhat larger in 10PE33 with 124% versus 78% added water when compared at equal amounts of nonfreezing water. An explanation for this difference is lacking. However, it is possible to suggest why the depression of the glass transition temperature by water is less efficient in the block copolymer soft-segment samples. Because the poly(ethylene oxide) in these samples is present as the endcapping segment, it consists of a small number of repeat units: only 11 in 5PEO and 7 in 3PEO compared with 36 in 10PEO. Mobility in these poly(ethylene oxide) end segments will be restricted by the attachment through the urethane linkage to the rigid hard-segment structure. It might also be restricted by a lack of swelling of the more hydrophobic phase-segregated poly(propylene oxide) component. These restrictions on mobility are not a consequence of intermolecular interactions and, therefore, would not be expected to respond as vigorously to the increased free volume contributed by the added water. This explanation suggests that the results for the pure poly(ethylene oxide)-containing sample represent a better test of the mixing and the free-volume relations for the depression of the glass transition temperature. In this respect, it is interesting that the addition of water results in such a large reduction of the glass transition temperature of the poly(ethylene oxide)-based sample, since there is evidence that there are very strong interactions between water and poly(ethylene oxide), equivalent to a stoichiometry of 3 mol of water per ethylene oxide unit.¹²

The glass transition temperature of poly(ethylene oxide) is not known with certainty. However, when incorporated into polyurethane, an increase in the glass transition temperature is expected. At least in part, this change is due to mixing of short urethane segments with the soft-segment phase, which results in hydrogen bonding between the miscible urethane groups and the ether oxygen of the soft segment. Thus, in addition to the free-volume contribution, the effectiveness of water in lowering the glass transition temperature might be due to a reduction in the urethane-to-ether hydrogen bonding. If this effect could be taken into account, it should permit fitting of the 10PE33 data by the free-volume expression with somewhat lower values of the thermal expansion coefficient for water. However, this value is so large that it would probably still lie outside the physically acceptable range.

CONCLUSIONS

The DSC examination of the state of water in the various samples as a function of equilibration temperature indicates that the depression of the glass transition temperature is controlled by the amount of nonfreezing bound water, with very little contribution from the other forms of water. It is somewhat surprising that the bound freezing water, which is present in considerable amounts under certain conditions, has so little effect. Moreover, there is a striking difference in the effect that the nonfreezing bound water has in lowering the glass transition temperature of the two types of samples. The effect is much larger in the sample with the pure poly(ethylene oxide) soft segment than in the samples with block copolymer soft segments. As a consequence, it cannot be expected that any single relation will provide an equally close fit to the results for both types of samples. It is suggested that this difference arises from the short length of the poly(ethylene oxide) segments, which are the terminal segments in the block copolymer soft segment, and from the restrictions on mobility due to coupling to the rigid hard-segment units as well as to the unswollen poly(propylene oxide) segments. It is not expected that these restrictions to mobility would be offset by the free volume contributed by the added water.

The comparison of the predicted values of the glass transition made with the simple Fox mixing relation, using a water T_g of 137 K, shows that there is a good fit to the experimental values for 10PE33 with 124% added water [grams of water per 100 g poly(ethylene oxide)]. However, this relation seriously overestimates the depression of the glass transition temperature for the block copolymer soft-segment samples. Use of the alternate value of 165 K for the water T_g provides a better fit to the data for 10PE33 with 78% water and a somewhat closer estimate of the glass transition temperatures of the other samples. Nevertheless, this finding cannot be taken as evidence favoring the higher glass transition temperature for water, because of uncertainties in the data. This is exemplified by the difference in the T_g depression in 10PE33 for the two levels of added water when compared at equal amounts of nonfreezing water.

Analyses using the free-volume relation provide a better fit to the data for the block copolymer samples than for the pure poly(ethylene oxide) sample, with a water thermal expansion coefficient in the range of 2.0×10^{-4} or 3.0×10^{-4} , depending on

whether the lower or higher T_g is used for water. An unacceptably high value of the thermal expansion coefficient is required to obtain a close match to the depression of the glass transition temperature for 10PE33 with 78% water. Nonetheless, in view of the effects mentioned above involving the restriction to the mobility of the block copolymer soft segment, it appears that the results for 10PE33 are to be preferred in testing the predictive relations for the diluent depression of the glass transition temperature. On this basis, the simple Fox mixing equation is more useful than is the free-volume relation used here. But this study also indicates the need for more reliable data, especially on the state of water and the depression of the glass transition temperature in the samples based on the pure poly(ethylene oxide). In addition to the DSC measurements, solid-state NMR could be useful in defining the state of the added water and its effect on polymer mobility.

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