Enthalpy Relaxation in Poly(propylene oxide)/Poly(ethylene oxide) Blends

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ABSTRACT: Phase behavior in poly(propylene oxide)/poly(ethylene oxide) blends was studied by glass transition observations in conjunction with enthalpy relaxation technique. The results points out that the blend behaves as an immiscible, phase separated system, nevertheless the displacements of the glass transition temperatures together with the results obtained from enthalpy relaxation experiments show that a polymer–polymer interaction is present.

KEY WORDS Enthalpy Relaxation / Poly(propylene oxide) / Poly(ethylene oxide) / Blends / Differential Scanning Calorimetry /

Ionically conducting polymers¹ are currently of intense technological interest for a wide variety of potential applications, particularly in high-energy density batteries, and electrochemical and electrochromical devices.² Conduction occurs primarily through amorphous regions of the polymer^{3,4} with ionic association and segmental motion of the polymer backbone playing a major role. Physical ageing in polymeric systems is the term used to describe the time dependence of changes in the behaviour of an amorphous polymer held at temperatures below the glass transition; such changes are normally the result of continuous slow relaxation of the glass from its initial non-equilibrium state towards its final thermodynamic equilibrium state. Aging affects a large number of properties such as density, modulus and the rate of stress, strain, enthalpy, and volume relaxations.^{5–7}

In a recent paper Cowie and Ferguson⁸ found that the total amount of enthalpy relaxation in the miscible polystyrene/poly(vinyl methyl ether) is much lower than for the pure components, measured at comparable undercoolings relative to the glass transition temperatures. In this paper we will consider

enthalpy relaxations in blends of poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO). Both polymers are known to be miscible when low molecular weight, the blend being immiscible as chain length increases.⁹

EXPERIMENTAL

Poly(propylene oxide) was obtained from Zeon Chemical Inc. (PAREL 58). This elastomer is a sulphur vulcanizable copolymer of propylene oxide and a 5% of allyl glycidil ether. As the primer constituent is propylene oxide, this material will be referred throughout this paper as PPO. The polymer was purified by a precipitation procedure and dried under vacuum at 323 K for 48 hours. Poly(ethylene oxide) was purchased from Aldrich (Ref 18.947-2) and was used as received. Blends of different compositions were obtained by casting from acetonitrile solutions.

Heat capacity (C_p) measurements were performed in a Mettler TA4000 differential scanning calorimeter. For annealing experiments the samples were kept at a temperature of 373 K for ten minutes to erase the thermal history, then cooled to the annealing tempera-

ture (193 K), annealed at this temperature for various amounts of time (30–480 min), cooled to 133 K, and finally reheated to 373 K at a heating rate of 10 K min⁻¹. After keeping the samples at 373 K for ten minutes, a second scan was taken over the same temperature range.

For cooling experiments each sample was kept in the calorimeter cell at 373 K for ten minutes, cooled at one of five cooling rates (1, 2.5, 5, 10, or 20 K min⁻¹) and immediately reheated over the same temperature range at a heating rate of 10 K min⁻¹.

RESULTS AND DISCUSSION

Glass transition temperatures, taken at the midpoint of the DSC jump are listed in Table I for the annealed samples as a function of time. First of all, it has to be pointed out that annealing time does not have a remarkable effect on the glass transition temperature. Two transition were observed, attributable to the two components of the blend, thus indicating that the blend behaved as a immiscible, phase-separated system. However, T_g 's are displaced related to the pure polymers, suggesting the existence of some degree of polymer–polymer interaction.

The kinetics of the processes in the glass transition region is both nonexponential and nonlinear. The relaxation toward equilibrium can be described well by the Kohlrausch–Williams–Watts nonexponential function $\phi(t)^{10}$

given by:

$$\phi(t) = \exp[-(t/t_c)^\beta] \quad (1)$$

The exponential function $\phi(t)$ was determined experimentally from enthalpic data using the Cowie–Ferguson model¹¹:

$$\Delta H(t_a, T_a) = \Delta H_\infty(T_a)[1 - \phi(t_a)] \quad (2)$$

The parameters $\Delta H_\infty(T_a)$, t_c , and β were determined by using a nonlinear regression analysis. $\Delta H_\infty(t_a, T_a)$ corresponds to the excess enthalpy lost on aging at a temperature T_a for an aging time of t_a minutes, t_c is a characteristic time, and β is the nonexponentially parameter ($0 < \beta < 1$), related to the width of the underlying relaxation time spectrum for the enthalpic aging process.

In order to measure $\Delta H(t_a, T_a)$, a difference heat capacity curve $C_p(T) = C_{p,aged}(T) - C_{p,unaged}(T)$ was constructed using C_p data from an aged and unaged sample and this was then integrated between selected limits in order to obtain $\Delta H(t_a, T_a)$. Several measurements of $\Delta H(t_a, T_a)$ at the same aging time were made to ensure that the results were reproducible.

Figure 1 show the relaxation behavior of annealed poly(propylene oxide). To facilitate comparison, experimental heat capacity data were normalized to the dimensionless C_p^N defined as:

$$C_p^N = \frac{C_p(T) - C_{p,g}(T)}{C_{p,e}(T) - C_{p,g}(T)}$$

Table I. Glass transition temperatures (K) of PPO/PEO blends annealed at 193 K

PPO/PEO wt%	$t_a = 30$ min		$t_a = 60$ min		$t_a = 120$ min		$t_a = 240$ min		$t_a = 480$ min	
	T_g^{PPO}	T_g^{PEO}	T_g^{PPO}	T_g^{PEO}	T_g^{PPO}	T_g^{PEO}	T_g^{PPO}	T_g^{PEO}	T_g^{PPO}	T_g^{PEO}
100/0	208.1	—	207.9	—	208.3	—	208.1	—	209.0	—
90/10	207.7	—	207.8	—	207.6	—	208.5	—	208.4	—
80/20	207.0	220.7	207.4	226.5	207.5	—	207.9	—	208.5	—
70/30	207.2	220.8	206.9	223.2	207.5	223.8	208.3	222.4	208.3	—
60/40	208.6	222.3	208.9	222.4	209.2	225.5	209.4	229.4	210.1	—
40/60	207.4	220.2	207.8	221.4	207.0	227.4	207.7	221.7	208.5	221.7
20/80	205.2	217.8	206.5	217.9	206.6	219.7	206.6	219.3	207.6	220.8
0/100	—	216.8	—	216.8	—	216.8	—	216.9	—	216.9

Figure 1. Normalized heat capacity data for PPO after annealing at 193 K for the indicated times.

Figure 2. Normalized heat capacity data for PPO/PEO 60/40 blend annealed at 193 K for the indicated times.

where $C_{p,g}$ is the glass heat capacity well below the relaxation temperature range (linearly extrapolated into the transition regime) and $C_{p,c}$ is the liquid (or rubber) heat capacity (similarly extrapolated).

The results show a broadening of the glass transition region as annealing time increases, while the temperature of the peak maxima is independent of time. Blends show a similar

Figure 3. Normalized heat capacity data for PPO/PEO blends annealed at 193 K for 60 min.

Figure 4. $\Delta H(t_a, 193)$ versus t_a for PPO. Lines are the theoretical fit to the Cowie-Fergusson model.

behaviour (Figure 2). Figure 3 shows normalized C_p for the different blends annealed at 193 K during 60 min; the peak maxima temperature is practically independent of blend composition, a displacement towards lower temperatures being observed for the PPO/PEO 20/80 blend, while the area under the peak decreases as PEO concentration in the blend grows up. Figure 4 shows the experimental $\Delta H(t_a, 193)$ vs. annealing time data obtained for poly(propylene oxide) together with the

Table II. $\Delta H(t_a, 193 \text{ K})$ (J g^{-1}) and peak temperatures (K) for annealed PPO/PEO blends

PPO/PEO	$t_a = 30 \text{ min}$		$t_a = 60 \text{ min}$		$t_a = 120 \text{ min}$		$t_a = 240 \text{ min}$		$t_a = 480 \text{ min}$	
wt%	$\Delta H/\text{J g}^{-1}$	T/K	$\Delta H/\text{J g}^{-1}$	T/K	$\Delta H/\text{J g}^{-1}$	T/K	$\Delta H/\text{J g}^{-1}$	T/K	$\Delta H/\text{J g}^{-1}$	T/K
100/0	1.09	211.6	1.41	211.5	1.59	211.2	2.41	212.1	2.78	212.1
90/10	1.12	211.1	1.34	211.0	1.65	211.1	1.95	211.5	2.63	211.4
80/20	1.14	210.8	1.29	211.5	1.93	211.5	2.42	210.9	2.87	211.8
70/30	0.93	210.5	1.58	210.5	1.90	210.3	2.30	211.2	2.86	212.2
60/40	0.92	211.9	1.45	213.1	1.82	213.5	2.30	213.5	3.15	213.5
40/60	0.90	209.7	1.69	210.9	2.17	211.7	2.74	211.7	3.88	211.7
20/80	0.99	208.8	1.65	208.6	2.84	209.3	4.89	209.8	6.02	210.7

solid curve obtained from the regression analysis. Table II listed the enthalpy $\Delta H(t_a, T_a)$ data obtained as well as the peak maxima temperatures. The data show that at low annealing times, enthalpy relaxation increases slightly and then decreases as PEO concentration in the blend increases. At high annealing times, enthalpy relaxation remains constant and then increases when PEO concentration in the blend is higher than 30 wt%.

Based on this $\Delta H(t_a, T_a)$ data, and applying equations 1 and 2, the three parameters $\Delta H_\infty(T_a)$, t_c , and β were determined. Values are shown in Table III. $\Delta H_\infty(T_a)$ and the characteristic time t_c remain practically unaltered up to a PEO concentration in the blend of 30 wt%, then increases as a result of the increase of the degree of polymer-polymer interaction.

Glass transition temperatures obtained from cooling experiments show similar behaviour to that previously founded for annealed samples. Two glass transitions were obtained (Table IV), again displaced regarding to the pure polymers. The PEO/PPO 20/80 blend show a single glass transition (miscible blend) at high cooling rates, when low cooling rates allow the system to be phase separated leading to two separated glass transitions. Figure 5 show the normalized C_p^N vs. cooling rate data obtained for poly(propylene oxide) and Figure 6 show the variation of ΔH with the reciprocal of the cooling rate. Again the position of the peak remain constant,

Table III. Numerical data obtained for PPO relaxation kinetics of samples annealed at 193 K

PPO/PEO	ΔH_∞ (193 K)	$\log t_c$	β
wt%	J g^{-1}	min	
100/0	6.25	3.20	0.42
90/10	5.32	3.14	0.40
80/20	6.25	3.16	0.42
70/30	5.74	3.06	0.42
60/40	14.4	4.07	0.44
40/60	19.9	4.07	0.48
20/80	33.0	4.18	0.48

independent of cooling rate, while ΔH increases as v_c decreases. Blends present the same behaviour (Figure 7), being the peak area decreasing as PEO concentration in the blend increases. It has to be pointed out that the values obtained from the enthalpies are much lower than those obtained from the annealing experiments. A compilation of enthalpy relaxation data obtained from cooling experiments are shown in Table V. The value of $\Delta H(v_c)$ decreases as cooling rate increases for all samples. Relating to blend composition, $\Delta H(v_c)$ remains practically unaltered at low cooling rates when PEO concentration in the blend is lower than 20 wt%, and then decreases as PEO concentration increases. At high cooling rates, the values of $\Delta H(v_c)$ are low, so it is difficult to establish any relationship as a results to the experimental errors.

Table IV. Glass transition temperatures (K) of PPO/PEO blends quenched at different cooling rates

PPO/PEO	$v_c = 1 \text{ K min}^{-1}$		$v_c = 2.5 \text{ K min}^{-1}$		$v_c = 5 \text{ K min}^{-1}$		$v_c = 10 \text{ K min}^{-1}$		$v_c = 20 \text{ K min}^{-1}$	
wt%	T_g^{PPO}	T_g^{PEO}	T_g^{PPO}	T_g^{PEO}	T_g^{PPO}	T_g^{PEO}	T_g^{PPO}	T_g^{PEO}	T_g^{PPO}	T_g^{PEO}
100/0	208.8	—	208.8	—	208.9	—	208.9	—	209.1	—
90/10	208.1	—	208.5	—	208.0	221.3	208.3	—	208.3	221.7
80/20	208.1	—	208.0	—	208.5	220.7	208.5	—	208.7	220.1
70/30	208.0	222.9	207.9	220.3	207.9	221.3	207.8	222.4	208.7	222.5
60/40	209.5	222.6	210.1	221.5	209.8	—	209.8	229.4	210.6	—
40/60	207.9	219.1	208.4	218.2	208.5	—	208.8	221.7	209.0	—
20/80	206.0	216.8	207.2	216.7	211.6		211.6		210.9	
0/100	—	214.9	—	214.8	—	215.8	—	215.8	—	216.8

Figure 5. Normalized heat capacity data for PPO after cooling at the indicated cooling rate.

From annealing and cooling experimental data it is apparent that aging studies are an additional useful technique to study polymer–polymer miscibility. At first sight, the value of the enthalpy difference between the aged and unaged samples is related to two factors, polymer–polymer interaction and diffusion. When diffusion increases (in our case by increasing PEO concentration in the blend), this will lead to a lower value of $\Delta H(t_a, T_a)$, which would explain the results at low annealing times. When polymer–polymer interactions develop, this will be traduced in an increase in the value of the enthalpy. So, we

Figure 6. $\Delta H(t_a, 193)$ versus $1/v_c$ for PPO. **Figure 7.** Normalized heat capacity data for PPO/PEO 60/40 blend after cooling at the indicated cooling rate.

Table V. $\Delta H(v_c)$ and peak temperatures for quenched PPO/PEO blends

PPO/PEO	$v_c = 1 \text{ K min}^{-1}$		$v_c = 2.5 \text{ K min}^{-1}$		$v_c = 5 \text{ K min}^{-1}$		$v_c = 10 \text{ K min}^{-1}$		$v_c = 20 \text{ K min}^{-1}$	
wt%	$\Delta H/\text{J g}^{-1}$	T/K	$\Delta H/\text{J g}^{-1}$	T/K	$\Delta H/\text{J g}^{-1}$	T/K	$\Delta H/\text{J g}^{-1}$	T/K	$\Delta H/\text{J g}^{-1}$	T/K
100/0	1.41	212.2	1.05	212.2	0.77	212.2	0.36	212.2	0.14	213.2
90/10	1.49	211.6	1.06	211.6	0.70	211.7	0.25	211.7	0.30	211.8
80/20	1.44	211.0	0.74	212.0	0.54	212.0	0.20	211.1	0.08	213.1
70/30	1.22	211.3	0.68	211.3	0.55	211.4	0.45	211.4	0.09	211.4
60/40	1.36	212.6	0.52	213.5	0.22	213.6	0.17	214.6	—	—
40/60	1.01	211.7	0.46	210.7	—	—	—	—	—	—
20/80	1.11	208.8	0.41	209.8	—	—	—	—	—	—

can establish that for low interacting polymer blends, like the system PPO/PEO, the enthalpy relaxation process is highly controlled by diffusion effect, the polymer-polymer interaction been manifested at long annealing times. Further work in highly interacting polymer blends is conducted to confirm this postulate.

CONCLUSIONS

Glass transition and enthalpy relaxation behavior in blends of poly(propylene oxide) and poly(ethylene oxide) were investigated. From the results obtained it can be established that the blend behaves as a immiscible, phase-separated system, nevertheless the displacements of the glass transition temperatures together with results obtained from enthalpy relaxation experiments show that a polymer-polymer interaction is present.

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