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A Dilatometric Study of Compatible Polymer Mixtures

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Polymer mixtures of poly(vinyl nitrate) ($PVONO_2$), and poly(vinyl acetate) (PVOAc), which had previously been concluded to be compatible with each other, were investigated by the dilatometric method. As a result, a characteristic behavior of the mixtures was observed. Each mixture showed a single glass-transition temperature (T_g) over the whole range of composition; this temperature was higher than those of pure polymers in the middle region of composition. The transition temperatures of the mixtures obeyed a modified Gordon-Taylor expression. The thermal expansion coefficients of the mixtures are discussed in relation to the effect of blending.

The investigation of compatible polymer mixtures is quite interesting as a means to know the possible behavior of polymer mixtures and to achieve a proper definition of compatibility.

There are only few polymer pairs which are compatible with each other. Especially, it is very difficult to make a compatible mixture with a pair of chemically-different polymers over a whole range of composition. Bohn[1] recently listed, from literature, thirteen examples of polymer pairs for which compatibility has been established, at least over a certain composition range. Among those polymers which are chemically quite different from each other, there are only a few pairs in which the compatibility is established over the whole range of their compositions. These are PVC(polyvinylchloride)/NBR(arcylonitile butadiene rubber)[2,3] and natural rubber/poly(butadiene)(Russian SKB).[4]

Other reports have shown by means of dynamic mechanical study[5] and by studying the heat of mixing[6,7] that PVOAc/nitrocellulose and PMMA (polymethyl methacrylate)/nitrocellulose are compatible pairs while the PIPA(polyisopropyl acrylate)/PIPMA(polyisopropyl methacrylate) pair has been established by dilatometric study[8] and the SBR(styrene butadiene rubber)/BR(butadiene rubber)[9] and phenol resin/NBR[10] pairs, by dynamic mechanical study.

We have studied the compatibility of mixtures of $PVONO_2$ and PVOAc. Several data, such as the temperature variation in the refractive indices and the mechanical properties ($T_{D\max}$), together with the observation under a phase-contrast microscope, have been taken to confirm the compatiblity of these mixtures, and it has been concluded that compatibility is observed in this pair with regard to these properties.[11,12]

In this paper, the thermal expansion of the polymer mixtures was investigated with dilatometers which are of the same type as that constructed by Bekkedahl.[13] In this dilatometric study, the present author also found that the glass-transition temperatures of the mixtures are slightly higher than those of the pure polymers. In addition, it is shown that the glass-transition temperatures of the mixtures satisfy the modified Gordon-Taylor equation introduced by Jenckel[14] and by Uematsu[15] for the copolymer system [Eq. (1)]:

$$T_{g12} = \frac{W_1\Delta\alpha_1 T_{g1} + W_2\Delta\alpha_2 T_{g2}}{W_1\Delta\alpha_1 + W_2\Delta\alpha_2} + \frac{W_1 W_2 \Delta k}{W_1\Delta\alpha_1 + W_2\Delta\alpha_2} \qquad (1)$$

where T_{g12} is the glass-transition temperature of the mixture containing the weight fractions, W_1 and W_2, of two pure polymers, whose glass-transition temperatures are T_{g1} and T_{g2} respectively.

$$\Delta\alpha_1 = \alpha_{l1} - \alpha_{g1},\ \Delta\alpha_2 = \alpha_{l2} - \alpha_{g2} \text{ and } \Delta k = \bar{k} - k.$$

α_g and α_l are the volume expansion coefficients in the glassy and liquid states respectively. The 1 and 2 subscripts refer to two pure polymers, 1(PVOAc) and 2($PVONO_2$). $\bar{k}$ and k are parameters representing the volume change on mixing, as expressed by the following equations:

$$\begin{aligned}\bar{V} &= W_1\bar{V}_1 + W_2\bar{V}_2 + \bar{k}W_1W_2 \\ V &= W_1V_1 + W_2V_2 + kW_1W_2 \qquad (2)\end{aligned}$$

where $\bar{V}$ and V are the specific volumes of a mixture in the glassy and liquid states respectively. The change in the specific volume with the temperature is assumed to be linear.

Experimental

The poly(vinyl nitrate) ($PVONO_2$) used for this work was obtained by the nitration[11] of a commercial sample of poly(vinyl alcohol) (PVA) with a degree of polymerization (DP) of 1700. The degree of nitration was 94.8 mol%. The poly(vinyl acetate) (PVOAc) used was a purified sample of a commercial product with a DP of 1800. Five specimens of polymer mixtures, BII-1, -3, -5, -7, and -9, were prepared from mixed solutions of $PVONO_2$ and PVOAc by evaporating the solvent. The mixing ratios of $PVONO_2$ to PVOAc in these samples were, in weight, 9/1, 7/3, 5/5, 3/7, and 1/9

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respectively, as is shown in Table 1. The conditions of preparation were given in detail in earlier reports.[11,12]

The specific volume of each specimen was measured at 25°C by the density gradient method. An aqueous solution of $CdCl_2$ was used for $PVONO_2$, BII-1, -3, and -5, and a $CaCl_2$ solution, for BII-5, -7, -9, and PVOAc. The temperature variation in the specific volume was determined by a method well-known in dilatometry.[13]

Dilatometry. The dilatometers were constructed of Pyrex glass and had a reservoir volume of about 20 cc. The measuring section was constructed of a precisely-bored capillary tube with a cross section of 0.01640—0.01642 cm^2. Each capillary was checked for uniformity and was calibrated with a mercury bead by the use of a travelling microscope. The volume of the reservoir was also determined by calibration with mercury. Tiny pieces of polymer samples without a void were cut off, weighed amounts of the tiny films were placed into the dilatometers, and then glass tubes were carefully shielded in order not to pyrolyze them. A special-grade commercial mercury was then charged on the top of the polymer samples while it was still under a vacuum. After breaking the vacuum, the mercury-filled dilatometers were allowed to rest for more than 24 hr at room temperature. They were then put into a water-ice bath maintained at 0——3°C. After a temperature equilibrium had been established, the temperature was raised at a rate of 20°C/hr and readings taken at 1°C intervals on a cathetometer which could be read to 0.005 cm. The glass-transition temperatures (T_g) and the volume-expansion coefficients below T_g (α_g) and above T_g (α_l) were obtained by this dilatometric measurement at the temperature elevation rate of 0.3—0.5 deg/min. The average standard estimations of the error in dv/dT were 1.5×10^{-6} cc/g°C in the glassy region and 3.0×10^{-6} cc/g°C in the rubbery region. The obtained T_g values were defined as the intersection of the straight-line portions of the plots of the specific volume *versus* the temperature.

Results and Discussion

Figure 1 shows the specific volume-*versus*-temperature curves obtained for $PVONO_2$, BII-1, BII-3, BII-5, BII-7, BII-9, and PVOAc. In the case of $PVONO_2$, it is noteworthy that the expansion does not show a linear increment above 55°C on account of the thermal degradation of $PVONO_2$. Table 1 summarizes the values of dv/dT, α_g, α_l, and T_g for the samples used. The calculated values for T_g were obtained from Eq. (1) using the following values:

$$T_{g1} = 302.4\text{°K (PVOAc)},\quad T_{g2} = 303.1\text{°K (PVONO}_2\text{)},$$

$$\alpha_1 = 2.88\times10^{-4},\ \alpha_2 = 5.09\times10^{-4},\ \text{and}\ \Delta k = 0.0097.$$

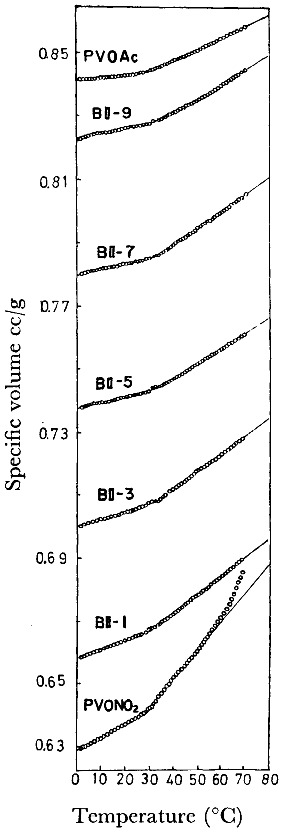

Fig. 1. Thermal expansion of $PVONO_2$, PVOAc, and mixtures.

To obtain the Δk value, we first read off a set of the values of the specific volume, $\bar{V}$ and V, say, at 0°C in the glassy state and at 50°C in the rubbery state, from the curves in Fig. 1. These values of $\bar{V}$ and V are plotted against W_1W_2 in Fig. 2. Then, we obtain, from the slopes of the straight lines, $\bar{k}=0.0205$ (cc/g) and $k=0.0108$; hence, the value of $\Delta k=0.0097$ is obtained [see Eq. (2)].

Figure 3 shows the glass-transition temperature, T_g, as a function of the weight fraction of PVOAc in the mixture. The full curve represents the calculated values of T_g given by Eq. (1), while the black and open circles are the experimental values obtained from the temperature dependencies of the refractive indices[11] and of the specific volumes respectively. It may be seen that the theoretical curve is in better agreement with the values obtained from the refractive indices.

Table 1. Transition temperatures of $PVONO_2$ and PVOAc mixtures

Samples	Weight ratio of $PVONO_2$/PVOAc	Specific volume at 25°C cc/g	Expansion coefficient (dv/dT) cc/g°C			$T_g^{dil.}$ °K a)	$T_{g}^{n_D}$ °K b)	$T_g^{cal.}$ °K c)
			Below T_g $\alpha_g\times10^4$	Above T_g $\alpha_r\times10^4$	($\Delta\alpha=\alpha_r-\alpha_g$) $\times10^4$			
$PVONO_2$	10/0	0.6396	4.51	9.60	5.09	303.1	304.0	(303.1)
BII-1	9/1	0.6659	2.90	6.10	3.20	304.0	304.7	304.8
BII-3	7/3	0.7063	2.16	5.75	3.59	305.0	307.0	307.1
BII-5	5/5	0.7421	1.88	5.18	3.30	306.3	308.2	308.5
BII-7	3/7	0.7844	1.88	5.21	3.33	306.0	307.4	308.2
BII-9	1/9	0.8265	1.50	4.61	3.11	304.0	304.0	305.3
PVOAc	0/10	0.8431	1.10	3.98	2.88	302.4	302.4	(302.4)

a) Obtained by dilatometric measurements. b) Obtained by refractometric measurements.[11] c) Calculated T_g from Eq. (1).

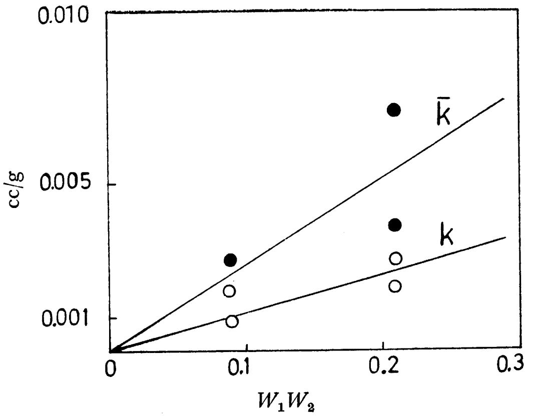

Fig. 2. Determination of $\bar{k}$ and k for PVONO$_2$ and PVOAc mixtures.
$\bar{V}-(W_1\bar{V}_2+W_2\bar{V}_2)$ and $V-(W_1V_1+W_2V_2)$ are plotted for W_1W_2 by Eq. (2).
From the slopes, $\bar{k}=0.0205$, $k=0.0108$ (cc/g).
(●, glassy state; ○, rubbery state)

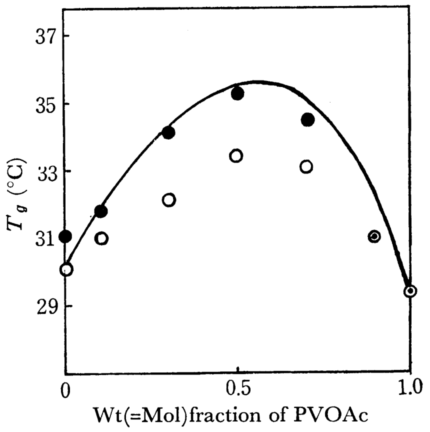

Fig. 3. Glass transition temperatures of PVOAc, PVONO$_2$, and their mixtures. The modified Gordon-Taylor expression is plotted using Eq. (1) (——). Experimental data obtained by means of refractometer (●) and by means of dilatometer (○).

Equation (2) appears to be insufficient to explain these experimental results completely. The small difference between the T_g values obtained by the two methods might be attributed to the errors due to the position of the thermometer and to the difference in experimental techniques (for example, the temperature-elevation rate). By the refractometric method we can avoid errors due to porosities in the samples better than by dilatometry; therefore, slightly higher values can be expected with the former method.

Figure 4 is a plot of the expansion coefficient as a function of the composition for the PVONO$_2$/PVOAc system. Small amounts of PVOAc can reduce the expansion of PVONO$_2$ quite effectively, but in the middle composition region, both α_g and α_l are nearly constant. It is clear that the α_g and α_l values of the mixtures deviate down from the straight lines. This depression in the expansion coefficients from additivity may result from an attractive interaction between the polar groups of the polymer pair.

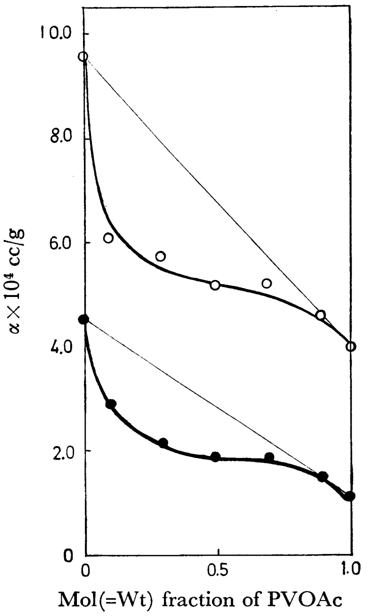

Fig. 4. Thermal expansion coefficients of PVONO$_2$, PVOAc, PVOAc, and their mixtures. (○, above T_g; ●, below T_g)

By other measurements, such as those by means of a phase-contrast microscope, by mechanical damping (by torsion pendulum[16]), and by the infrared spectra, the compatibility of this system has already been confirmed, and the characteristic behavior of the mixtures has been explained in forms of the interaction between the -ONO$_2$ and -OCOCH$_3$ polar groups. With the purpose of obtaining further evidence for this, studies of a low-molecular liquid mixtures of the nitric acid ester and the acetic acid ester, regarded as model compounds of the polymers, are now in progress by means of NMR and heat of mixing.

Recently Murakami[17] reported that a larger difference between the thermal-expansion coefficients of the homopolymers causes a rise in the T_g of the blend as a result of thermal stress. For the present compatible system, however it will be difficult to explain the results by this factor alone, although the large difference between the expansion coefficients may contribute to the rise in the T_g to some extent. As for the applicability of the Gordon-Taylor equation used for the copolymer in compatible mixtures, Koyama *et al.*[5] reported that, for the PVOAc/Nitrocellulose and PMMA/Nitrocellulose systems, the T_g varies with the composition according to this equation; Koleske and Lundberg[18] reported that the same was true for the poly ε-caprolactone/PVC system. However, Krause and Roman[8] found that, for PIPA/PIPMA mixtures, this equation was not applicable and argued that a new theoretical treatment was needed for their compatible mixtures. Therefore, by using only this equation it is quite difficult to determine whether or not they are compatible pairs.

By electron microscopic observations, Matsuo[19] re-

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cently showed that the PVC/NBR blends are not completely compatible and indicated that the micro heterogeneously-dispersed particles are less than 100 Å in diameter. Electron-microscopic observation will also be necessary to ascertain the morphology of this $PVONO_2/PVOAc$ system accurately.

From the studies of the $PVONO_2/PVOAc$ system, it is generally expected that the compatibility may be established when the intermolecular interaction between the mixed polymers has as strong an influence on the system as the intramolecular interaction.

Conclusions

By means of applying the dilatometric method to compatible mixtures of $PVONO_2$ and PVOAc, we arrived at the following conclusions:

(1) The mixtures showed higher glass-transition temperatures than both of the homopolymers.

(2) The transition data of the mixtures approximately obeyed the modified Gordon-Taylor equation.

(3) The fairly large depression of the expansion coefficients (Fig. 4) indicates the existence of a certain interaction between the polymer pairs.

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