

MODULUS-COMPOSITION DEPENDENCE FOR BLENDS OF PVC WITH SEGMENTED POLYURETHANES OF DIFFERENT SOFT SEGMENTS

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ABSTRACT

The dynamic mechanical modulus at 25 °C for blends of segmented polyurethanes with PVC was studied by using suitable mechanics models of multi-component systems. The analysis indicates that the blend morphology was mainly determined by soft segment structure of polyurethanes. The PPO-PU /PVC blends show typical two-phase morphology and their modulus-composition relations may be described by Halpin-Tsai model for domain-matrix two-phase systems. While the PCL-PU /PVC, PTMA-PU /PVC and PTMO-PU /PVC blends fit the Kerner's packed grain composite model. These results may imply that the modulus-composition relationship is sensitive to the interactions between the components and the mixture morphology of the blends.

INTRODUCTION

Blending of PVC with various types of polyurethanes has gained considerable technological value^[1]. It is also of scientific interest, since chloride containing polymers are reported to interact with oxygen containing polymers like polyurethanes through specific forces^[2]. Polyurethanes with soft segments of different chemical structure, average length and content have been studied by various authors^[3-12]. However discussion was usually only given on compatibility between PVC and the soft segments or on compatibility between PVC and the polyurethanes in general, and systematic studies on the relationship between morphology and properties of these blend systems were only given in a few cases. Kalfoglou^[1] reported the dynamic mechanical properties of blend of PVC and polyurethane over a wide temperature and composition ranges. The degree of mixture and /or interaction between the compositions was assessed using dynamic mechanical technique and the results were used to test the various models proposed to predict the properties of a polyblend from those of its pure components.

In the present work blends of PVC and four segmented polyurethanes with polyether or polyester soft segments of the same molecular weight (1000) and content were studied. The influence of soft segment structure on the morphology and properties of these multicomponent blends was discussed on the basis of various mechanics models for multicomponent systems.

EXPERIMENTAL

Materials

Segmented polyurethanes were synthesized by a two-step method involving

endcapping the hydroxy-terminated polydiols with 4, 4'-diphenylmethane diisocyanate (MDI) followed by reaction in solution with the chain extender, 1, 4-butanediol (BDO). The polydiols used were hydroxy-terminated polycaprolactone (PCL), poly(tetramethylene adipate) (PTMA), poly(tetramethylene oxide) (PTMO) and poly(propylene oxide) (PPO) of number average molecular weight 1000. The composition and intrinsic viscosity of the polyurethanes are given in Table 1. The intrinsic viscosity was measured in *N,N'*-dimethylacetamide at 30 °C. A suspension grade PVC was used, the molecular weight ($M_w = 15.3 \times 10^4$, $M_n = 5.7 \times 10^4$) of which was determined from GPC measurements.

Blends of PVC and polyurethanes were prepared by solution mixing in *N,N'*-dimethylformamide and they were cast into PTFE trays at 60–70 °C for evaporating solvents. Specimens were then dried in vacuum at 60 °C for at least a week to reach a constant weight and then kept in desiccator prior to use.

Table 1. Segmented polyurethane samples

Sample	Soft segment	Polyol / MDI / BDO*	$[\eta]$ (dl/g)
PU-12	PCL	1/2/1	0.95
PU-22	PTMA	1/2/1	0.75
PU-32	PTMO	1/2/1	1.02
PU-42	PPO	1/2/1	0.50

* The composition is in mole ratio.

Measurements

Dynamic mechanical measurements were performed at 3.3 Hz using an Iwamoto viscoelastic spectrometer. Samples were initially cooled down to about –180 °C, and measurements were conducted with a heating rate of 2–3 °C/min. The temperature range for measurements was from –180 °C to 100 °C.

MECHANICS MODELS FOR POLYMER BLENDS^[13–15]

The simplest rules for binary polymer blends correspond to the parallel and series connections, respectively, and give the following equations:

$$\text{parallel model} \quad P = P_1 \phi_1 + P_2 \phi_2 \quad (1)$$

$$\text{series model} \quad P = P_1 P_2 / (P_1 \phi_2 + P_2 \phi_1) \quad (2)$$

where P , P_1 and P_2 are the corresponding elastic modulus of blend components 1 and 2 respectively. ϕ_1 and ϕ_2 denote the volume fraction of components 1 and 2. In most cases the parallel and series models only serve as an estimate of the upper and lower bounds of the blend modulus.

Various kinds of elastic modulus of polymer can be related by the fundamental relations of elastic theory:

$$E = 3K(1 - 2\gamma) = 2G(1 + \gamma) \quad (3)$$

where E , K and G are the Young's modulus, bulk modulus and shear modulus, respectively and γ is the Poisson ratio.

For a two-phase system the elastic modulus is determined not only by the concentration and properties of its components, but also the state of mixture of the blend. There are many empirical formulae which may be used to predict the elastic modulus of blends of different types.

One of the well known formulae is that proposed by Kerner^[16] in 1956, which is based on the assumption that the inclusions are spherical and there is perfect adhesion between the phases. It gives the following form:

$$G_c / G_1 = [\Phi_1 G_1 + (\alpha_1 + \varphi_2) G_2] / [(1 + \alpha_1 \varphi_2) G_1 + \alpha_1 \varphi_1 G_2] \quad (4)$$

where

$$\alpha_1 = (8 - 10 \gamma_1) / (7 - 5 \gamma_1)$$

and subscripts c , 1 and 2 denote the blend, matrix and dispersed phase, respectively.

The Kerner's equation was widely used to predict the elastic modulus of copolymers, polymer blends and composites^[17-20]. But it did not offer much improvement than the parallel and series models.

Halpin et al.^[20-22] considered the maximum packing fraction φ_m of dispersed particles and obtained a modified Kerner's equation, i.e. the Halpin-Tsai equation. When the elastic modulus of matrix is greater than that of the dispersed phase, the Halpin-Tsai equation gives the form:

$$G_c / G_1 = (1 - B \psi \varphi_2) / (1 + AB \varphi_2) \quad (5)$$

where

$$A = (8 - 10 \gamma_1) / (7 - 5 \gamma_1), \quad B = (G_1 / G_2 - 1) / (G_1 / G_2 + A)$$

$$\psi = 1 + (1 - \varphi_m) \varphi_2 / \varphi_m^2$$

When the elastic modulus of the matrix is smaller than that of the dispersed phase, it gives the following equation:

$$G_c / G_1 = (1 + A' B' \varphi_2) / (1 - B' \psi \varphi_2) \quad (6)$$

where

$$A' = 1 / A, \quad B' = (G_2 / G_1 - 1) / (G_2 / G_1 + A')$$

Equations (5) and (6) fit the experimental data quite well in many cases of two-phase polymer blends.

Besides, there are many other empirical formulae predicting the elastic modulus of two-phase systems. One of those useful models is the Hashin's model which assumed that the dispersed particles are perfectly spherical, uniformly dispersed with no interaction, and it reduces to the expression^[23]:

$$K_c = K_m + (K_d - K_m)(4G_m + 3K_m) \varphi_d / [4G_m + 3K_d + 3(K_m - K_d) \varphi_d] \quad (7)$$

where subscripts c , m and d refer, respectively, to blend, matrix and dispersed phase properties, and φ_d is the volume fraction of the dispersed phase.

The equations discussed above were based on the assumption that the blends have well defined structure, i.e. a dispersed phase with a continuous matrix. Since blends do not have a well defined matrix, in which both components can be regarded as continuous, but which are nevertheless isotropic and macroscopically

homogeneous, a somewhat different approach is required. One method is based on the Kerner's packed grain composite model. A pair of simultaneous equations of G_c and K_c is obtained appropriately for a composite in which grains of species 1 and 2 are packed together randomly.

$$\varphi_1 (G_1 - G_c)(G_c + \alpha_c G_2) + \varphi_2 (G_2 - G_c)(G_c + \alpha_c G_1) = 0 \quad (8a)$$

$$\varphi_1 (K_1 - K_c)(K_c + \beta_c K_2) + \varphi_2 (K_2 - K_c)(K_c + \beta_c K_1) = 0 \quad (8b)$$

where

$$\alpha_c = (8 - 10\gamma_c) / (7 - 5\gamma_c) = 6(K_c + 2G_c) / (9K_c + 8G_c)$$

$$\beta_c = (1 + \gamma_c) / 2(1 - 2\gamma_c) = 3K_c / 4G_c$$

Faucher^[24] has applied equation (8) to the modulus-composition dependence of block copolymers, and excellent agreement was found between the experimental data and the predictions of the model.

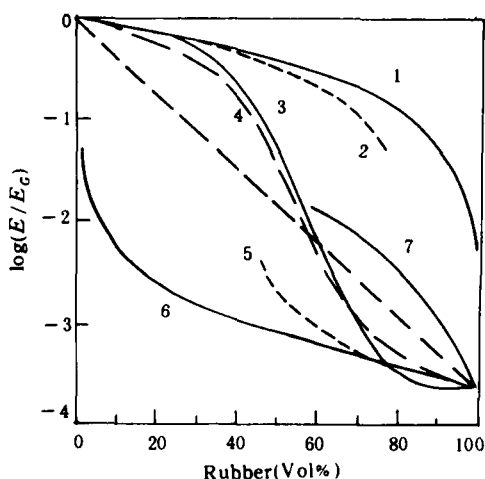


Fig. 1. Modulus-composition dependence for blends of a hard, glassy polymer and a soft rubber. Curves 1 and 6 are predicted by the original Kerner's equation. Curves 2 and 5 are typical experimental data for two-phase blends and the predictions of modified Kerner's equation. For curves 1 and 2 the glassy polymer is the continuous phase, for curves 5 and 6 the rubber is the continuous phase. Curve 3 shows the modulus-composition dependence for a series of homogeneous copolymers. Curve 4 is the prediction of the Kerner's packed grain composite model. Curve 7 is the prediction of Hashin's model with a rubber matrix. E_g is the Young's modulus of the glassy component.

While for one-phase binary mixture, it is necessary to consider the interaction between components. The most often used equation has the form:

$$P_c = P_1 \varphi_1 + P_2 \varphi_2 + I \varphi_1 \varphi_2 \quad (9)$$

where I refers to the interaction term.

Another very general and useful equation predicting the properties of one-phase binary mixtures is the so-called semilogarithm additive rule:

$$\text{Log } P_c = \varphi_1 \text{Log } P_1 + \varphi_2 \text{Log } P_2 \quad (10)$$

Equation (10) can also be used to the binary mixtures with two continuous phases due to its symmetric form.

Figure 1 summarizes the calculated data of equations mentioned, and typical experimental data of modulus for a rubber /glassy polymer blend are also given for comparison.

RESULTS AND DISCUSSION

In our previous studies^[25-26] the morphology of blends of segmented polyurethanes with PVC have been investigated in detail. It was found that the hard and soft segments are more mixed for polyester polyurethanes than for polyether ones. A large fraction of hard segments is separated individually in the polyester soft segment matrix. The polyester soft segments, especially the PCL segments, exhibit good mixture with PVC molecules in the blends, and it should be noted that the mixing of PVC molecules with polyester soft segments does not increase the segregation of the hard segments, but even more, in the blends of high PVC content the hard segments become more dispersed in the PCL soft segment matrix diluted by PVC molecules. Polyether based polyurethanes are much less mixed with PVC than the polyester ones. Blends of PVC with PU-42 can be

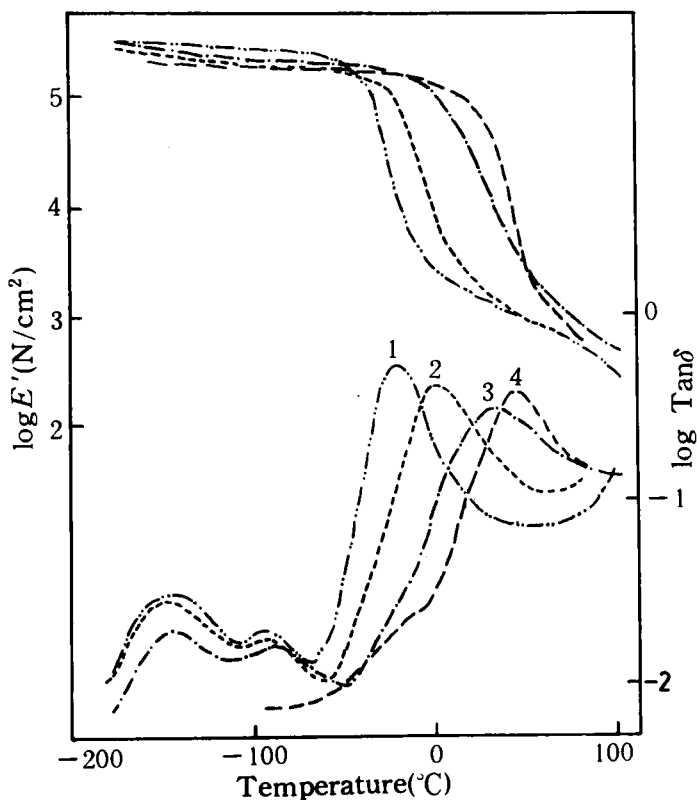


Fig.2 Dynamic mechanical curves of PU-12 / PVC blends with different blend ratio
1) 100 / 0; 2) 80 / 20; 3) 50 / 50 and 4) 20 / 80.

considered as completely unmixed two-phase systems, because two distinct T_g 's at exactly the same temperature positions of those of the two constituents respectively were observed, and the interaction between hard and soft segments of PU-42 was not influenced by blending with PVC. Blending of PVC and PU-32 also exhibit two T_g 's, but they are not at the same positions of those of the two components.

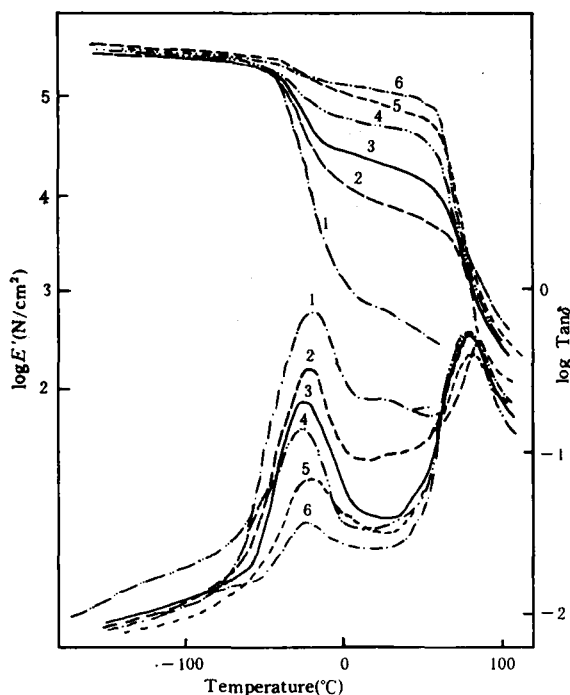


Fig. 3 Dynamic mechanical curves of PU-42/PVC blends with different blend ratio

1) 100/0; 2) 80/20; 3) 65/35; 4) 50/50; 5) 35/65 and 6) 20/80.

Dynamic mechanical modulus has been measured for all the blends in a temperature range from -180°C to 100°C . Results for blends of PU-12/PVC and PU-42/PVC are given in Figures 2 and 3. It is of great interest to compare our experimental data of blends, which exhibit quite different morphological features, with the modulus-composition relations predicted by different models. We can learn the validity of the various models and may probably get more information about the morphological details which have more influence on, or more expressed in, the mechanical behaviour of the blends.

Figures 4—7 show the dynamic modulus at 25°C as functions of composition of blends of PU-12/PVC, PU-22/PVC, PU-32/PVC and PU-42/PVC, respectively. Theoretical curves predicted by models of two-phase systems are also given in these figures. For calculating the elastic modulus the Poisson ratio γ of the blends was approximately taken as the arithmetic mean of those of their components weighted by their volume fractions, i.e.

$$\gamma_c = \gamma_1 \phi_1 + \gamma_2 \phi_2 \quad (11)$$

The Poisson ratios of PVC and polyurethane elastomers are taken as 0.35 and 0.49^[1,27], respectively.

It was expected that the series and parallel connection models can not describe the experimental data. The comparison of the results indicates that curves predicted by models based on assumptions of well defined domain /matrix morphology exhibit poor fit with the behaviour of the blend used, except the Halpin-Tsai equation which describes quite well the results of blends PU-42 /PVC, but not the others. It is clear from the figures that reasonable fits of experimental results with the packed grain composite model were obtained for the blend systems PU-12 /PVC, PU- 22 /PVC and PU- 32 /PVC. It implies that the modulus-composition relationship of blends is related to the interaction between components and hence the morphology, and it is possible to distinguish those blend systems from the others, the components of which may exist in the form of their own individual phases and do not have any special interactions between them except the volume exclusion effect and the force transfer ability at the phase boundaries within a limited stress or strain levels.

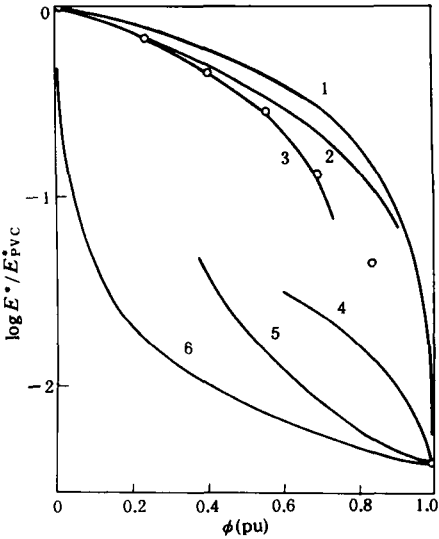


Fig.4 Comparison of calculated and experimental E/E_{PVC} values for PU-12 /PVC blends, -o- experimental data

Curves 1 and 6 correspond to parallel and series connection models, curve 2 is the prediction of Halpin-Tsai equation with PVC matrix and $\phi_m=0.8$, curve 3 corresponds to the packed grain model, curve 4 is the Hashin's model with PU matrix and curve 5 corresponds to the Halpin-Tsai equation with PU matrix and $\phi_m=0.64$

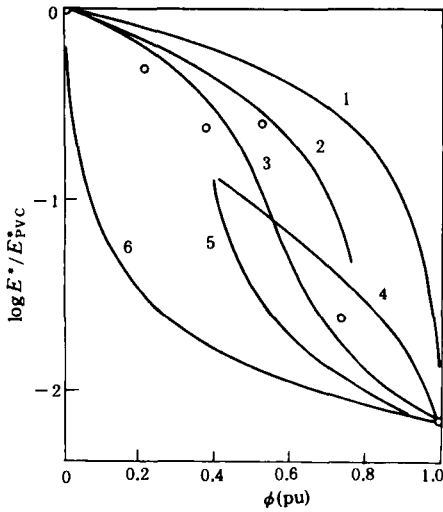


Fig.5 Comparison of calculated and experimental data of E/E_{PVC} for PU-22 /PVC blends

The meaning of the curves is the same as that in Figure 1

It has been reported that PVC and PCL homopolymers are miscible in their amorphous states. Our studies also showed good mixture between PCL soft segments and PVC molecules in blends PU-12/PVC, which may even improve the

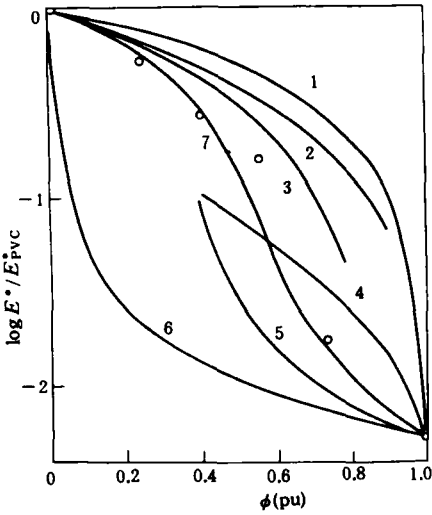


Fig.6 Comparison of calculated and experimental data of E/E_{PVC} for PU-32/PVC blends
The meaning of curves 1, 4, 5, 6 is the same as in Figure 4. Curve 2 is the prediction of original Kerner's equation, and curve 3 corresponds to the Halpin-Tsai equation with PVC matrix and $\phi_m=0.8$, curve 7 corresponds to the packed grain composite model.

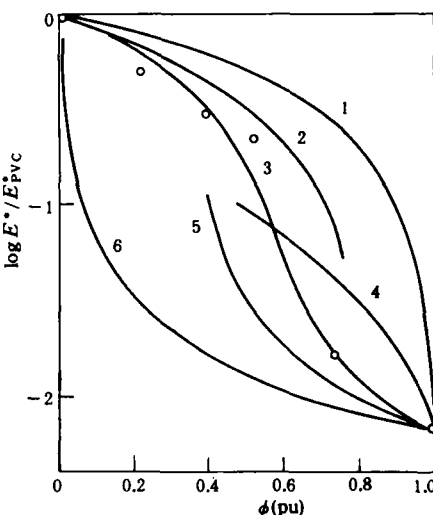


Fig.7 Comparison of calculated and experimental data of E/E_{PVC} for PU-42/PVC blends
The meaning of the curves is the same as in Figure 6.

dispersion of the hard segments. So it is interesting to check the behaviour of this blend system by the equations of miscible blends. Large deviations of experimental data from the empirical semi-logarithmic addition was observed in Figure 8. With appropriate selection of interaction parameter I equation (9) can more or less approach the data of low polyurethane content, but still fails in high polyurethane content region. It means that although the components of

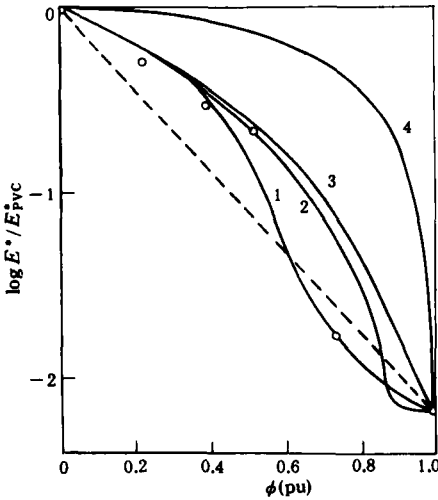


Fig.8 Comparison of experimental data of E/E_{PVC} for PU-12/PVC blends with Kerner's packed grain composite model (curve 1) and Equation 9 (curve 2: $I = -1.1 E_{PVC}$, curve 3: $I = -1.0 E_{PVC}$ and curve 4: $I = 1.0 E_{PVC}$)
Dash line denotes the semilogarithm additive rule

PU-12/PVC blends are very finely mixed, they should still be considered mechanically as multi-phase systems, rather than homogeneous phase systems of multi-components. Determination of mixture situation and miscibility of components is a basic and important problem in blend studies. Usually we can find out the interactions between the components by means of density, T_g , IR spectroscopy and many other techniques, however it remains difficult to ascertain the level of homogeneity of blend due to these interactions. Our results shown here imply that the modulus-composition relationship is sensitive in this point, and a combination of modulus measurements with other techniques may greatly benefit the understanding of morphological feature of multicomponent blends.

CONCLUSIONS

The behaviour of completely unmixed system PU-42/PVC can be described by the Halpin-Tsai equation. The Kerner's packed grain composite model may fit the results of the other three blends, the components of which are more or less interacted in blending. The modulus-composition relationship seems to be sensitive to the interactions between the components and the mixture morphology of the blends. Mechanical measurements are useful in ascertaining the completely unmixed and the homogeneous blends.

Keywords :

Blends ; Modulus ; Mechanics model ; PVC : Segmented polyurethane .

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