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# Compatible Glassy Polyblends Based Upon Poly(2,6-Dimethyl-1,4-Phenylene Oxide): Tensile Modulus Studies

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The mechanical behavior of compatible glassy polyblends based upon poly(2,6-dimethyl-1,4-phenylene oxide)(PPO) was investigated. In particular, the influence of composition, molecular weight, and molecular weight distribution upon the tensile modulus of the blend was assessed. Various possible correlations between the experimentally determined moduli and theory are considered. Included are correlations with density, packing density, composite theory, and lattice fluid theory. The modeling of the properties of mixtures via Simplex lattice design is also presented. Finally, attention is given to the development of compatibility criteria based upon tensile modulus and density measurements.

## INTRODUCTION

Blending of polymers is a widely used technique to improve rheological, mechanical, and degradative properties in polymers. Moreover, it affords the fabricator the opportunity to custom formulate a material to obtain desirable properties that may not be available in the homopolymers (1, 2). Finally, a polymer blend is often more economical than one of the homopolymers. For these reasons, the mixing of polymers is gaining increasing importance in the academic and industrial communities.

Among the blends receiving more attention recently are those composed of high molecular weight glassy polymers whose mixtures are truly miscible. Probably the best known and most successful example is based upon mixtures of PPO and atactic polystyrene (PS) (3) providing the basis for the family of engineering thermoplastics called Noryl (4). Although considerable mechanical data exists for these and other miscible polymer systems, little attention has been given to the modeling and correlating of their physical properties. Progress in this area ultimately should lead to the prediction of particular physical properties of the various compositional blends based upon the knowledge of only pure component properties.

It is the purpose of this paper to provide several possible correlations between the experimentally de-

termined modulus and theory. The discussion will be restricted, mostly, to the PPO-PS system; however, it should be possible to extend the theories presented to any two-component, glassy polymer alloys which remain compatible throughout their entire range of composition.

## EXPERIMENTAL

### Materials

The materials utilized in the making of the polymer blends were commercially available PPO and PS (HH 101). Narrow molecular weight distribution atactic PS was also utilized. The PPO and PS homopolymer molecular weights and their sources are summarized in *Table 1*.

### Sample Preparation

The PS homopolymers tabulated in *Table 1* were blended with PPO by coprecipitation from 3 weight percent toluene solutions into a 10:1 excess of methanol. The fine polymer powder in the methanol-toluene mixture was then filtered and dried in a vacuum oven for 48 hours at 100°C. Blends containing 25, 50, and 75 weight percent PPO were prepared in this manner.

The vacuum dried blend and pure component polymers were next injection molded via a Custom Scientific Instruments Mini-Max Molder (described in the recent literature) (5) into the form of tensile specimens. At least 20 samples of each blend composition were molded. Extreme care was taken to ensure that each sample at a

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Table 1. Summary of Molecular Weights

Narrow molecular weight distribution PS	Molecular weight	Polydispersity $\bar{M}_w/\bar{M}_n$	Source
PS-4,000	4,000	<1.06	Pressure
PS-10,000	10,000	<1.06	Chemicals
PS-37,000	37,000	<1.06	Company
PS-110,000	110,000	<1.06	
PS-223,000	233,000	<1.06	
PS-670,000	670,000	<1.15	
PS-2,000,000	2,000,000	<1.20	
HH 101 Monsanto polystyrene		$\bar{M}_n = 90,000-95,000$	
		$\bar{M}_w = 260,000-280,000$	
		$\bar{M}_z = 470,000-500,000$	
PPO General Electric		$\bar{M}_n = 17,000$	
		$\bar{M}_w = 35,000$	
		$\bar{M}_z = 54,000$	

particular composition experienced a controlled melt history.

### Tensile Testing

The injection molded tensile specimens were tested on a Tensilon/UTM-II mechanical tester. Measurements were made at room temperature at a constant cross-head speed of  $0.2 \text{ mm}\cdot\text{min}^{-1}$  on specimens with a gauge length of 8.9 mm. Suitable instrumental and clamp corrections were performed before calculating the modulus.

## RESULTS AND DISCUSSION

The modulus as a function of composition was obtained for a series of PPO-PS blends. In each series, the PPO had the same molecular weight and molecular weight distribution, while the PS had progressively higher molecular weight (see Table I). A typical modulus-composition relationship is depicted in Fig. 1 by the curve drawn through the experimental data.

Several features of the HH 101 PS-PPO modulus-composition relationship are particularly noteworthy. First, the modulus at each blend composition is higher than that which would be calculated by the simple "rule of mixtures":

$$E = w_1E_1 + w_2E_2 \text{ or } E = \phi_1E_1 + \phi_2E_2 \quad (1)$$

where subscript 1 refers to PS and subscript 2 refers to PPO, while  $E$ ,  $w$ , and  $\phi$  represent the modulus, weight and volume fractions, respectively. (In this case,  $\phi$  and  $w$  may be used interchangeably with negligible error since the density of each component differs by only 1.5 percent.) The rule of mixtures represents the upper bound in the modulus for a multiphase system. The lower bound in the modulus for a two-component system is represented by:

$$\frac{1}{E} = \frac{\phi_1}{E_1} + \frac{\phi_2}{E_2} \quad (2)$$

All other composite equations, such as the Kerner equation (6), the logarithmic rule of mixtures (7), and the Davies equation (8) will lie between curves B and C shown in Fig. 1. Clearly, no composite equation is able

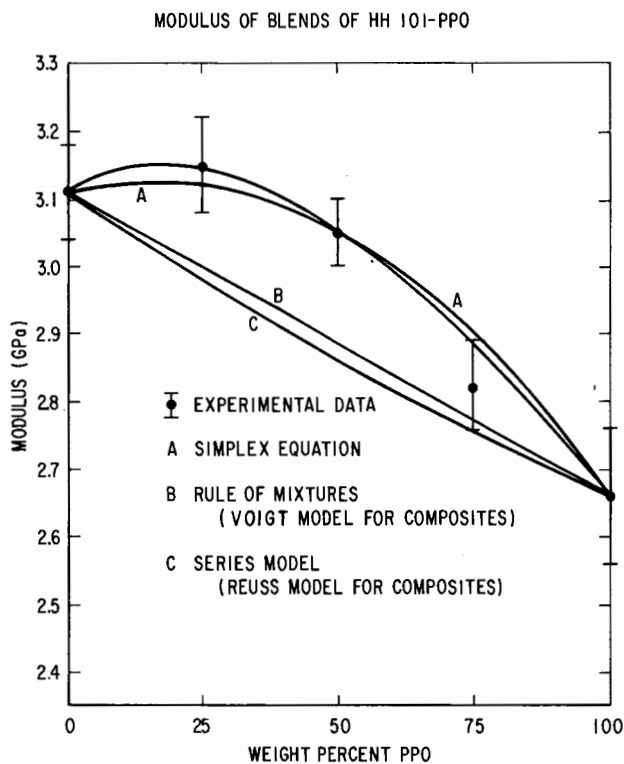


Fig. 1 Typical modulus-composition relationship for a PPO-PS blend.

to model the modulus of a glassy compatible polyblend or glassy polymer alloy. The term "alloy" here is used in its most restrictive sense: a physical mixture of two or more structurally different polymers exhibiting only a single  $T_g$  and showing synergistic improvement of the mechanical properties of the base resin (3). True polymer alloys are quite rare.

Not so rare are the synergistic improvements of the mechanical properties, such as the modulus, noted upon the addition of "antiplasticizer" to certain polymers such as PC, PS, and PVC (9-12). Other enhancements have been observed for some glassy-rubbery blends such as PVC blended with butadiene-acrylonitrile elastomers (13, 14). However, these effects are usually noted only for low "antiplasticizer" or rubber concentrations and not over the entire range of compositions, as is the case for glassy blends, such as PPO-PS.

Although composite equations fail to model the modulus for glassy alloys, Simplex equations can be generated which agree with the empirical data over the entire compositional range (15). Curve A in Fig. 1 is a representation of a second order polynomial for a two-component system. In terms of the modulus, the equation has the following form:

$$E = E_1 \chi_1 + E_2 \chi_2 + \beta_{12}^E \chi_1 \chi_2 \quad (3)$$

In this case,  $E_1$ ,  $E_2$ ,  $\chi_1$ , and  $\chi_2$  represent the moduli and compositions of PS and PPO, respectively. The interaction term,  $\beta_{12}^E$ , expresses the magnitude of the deviation from nonlinearity. A positive  $\beta_{12}^E$  represents a nonlinear synergism (criterion for compatibility?), while a negative  $\beta_{12}^E$  expresses a nonlinear antagonism (criterion for incompatibility?). The interaction term,  $\beta_{12}^E$ , can readily

be calculated (16, 17, 18) via

$$\beta_{12}^E = 4E_{12} - 2E_1 - 2E_2 \quad (4)$$

where  $E_{12}$  represents the response of the 50:50 mixture.

It is well known that compatibility decreases in compatible systems when the molecular weight of any of the components is increased (19). As can be noted from Fig. 2,  $\beta_{12}^E$  also decreases with increasing PS molecular weight. If  $\beta_{12}^E$  has some relationship with the "level of compatibility", the trend depicted in Fig. 2 is correct. Is then a positive  $\beta_{12}^E$  indicative of compatibility? The tentative answer is yes, as long as the polymer blend remains below the glass transition throughout the entire compositional range. Compatible mixtures of glassy-rubbery polymers also exhibit moduli above additivity (20), however, these mixtures cannot be modeled by a second order Simplex equation since at a particular composition (at  $T_g$ ), the modulus undergoes a catastrophic decrease. However, all reported glassy-glassy systems showing compatibility throughout their entire range of composition exhibit a positive  $\beta_{12}^E$ . Incompatible glassy systems do not exhibit such a modulus enhancement throughout their entire range of composition (21). Further verification of the significance of  $\beta_{12}^E$  lies in the obtaining of modulus data accurate to somewhat better than 1 percent. There can be considerable error (~20 percent) in the calculation of  $\beta_{12}^E$  since its value depends upon the subtraction of numbers of equal order of magnitude. Even with a 20 percent error, a trend similar to that shown in Fig. 2 would still be seen. Sonic modulus measurements would lead to greater accuracy in  $\beta_{12}^E$  (22).

Although Simplex equations can be generated to model modulus-composition empirical data, they give no indication of any correlation with molecular structure. A survey of the literature indicates that packing density, cohesive energy density and the glass transition temperature are, in the order given, the major factors that determine the numerical magnitude of the modulus (12). All three factors are interrelated. It is also important to consider the effect of secondary relaxations, at each of which the moduli make a step change, and the time scale of the imposed deformation used in calculat-

ing the moduli. These phenomena will exercise a blurring effect on correlation attempts.

The type of correlations for the modulus with respect to molecular structure one should attempt are easier to visualize if one recognizes that the elastic modulus at a particular temperature is composed essentially of two terms. The first term is the zero-point modulus, which in reduced form depends primarily upon the packing density. The other term consists of a negative temperature function, the magnitude of which is largely determined by the contribution of external degrees of freedom. These contributions include, among others, lattice heat capacities, internal rotation, and torsional oscillation (12). Such contributions are more readily lumped under the single term of background mechanical energy absorption and are manifested from a dynamic mechanical measurement yielding energy absorption vs time, frequency, or temperature. The modulus, however, will be altered (below  $T_g$ ) only by those secondary relaxations that also affect the free volume.

From the above discussion, one realizes that density and packing density are the key to understanding the modulus. This is particularly true for materials exhibiting no major secondary relaxational effects. Moreover, in reviewing the "antiplasticizer" literature (10-12) where maxima or enhancements in modulus vs antiplasticizer concentration have been shown to occur, one finds that the packing density of the polymer is the only equilibrium property that also passes through such a maximum. Since it appears that PS and PPO in the PS-PPO system behave in a manner similar to the "antiplasticization" phenomenon found in polymer-diluent systems, it is attractive to attempt various modulus-density correlations to ascertain their validity.

In Fig. 3, the modulus and density (21) (curves A and C, respectively) are both plotted as a function of PPO composition. Additionally, curves B and D illustrate the relationship one would expect if the modulus and density conformed to the "rule of mixtures." Because the location of the maxima of each of these two properties do not coincide, one might incorrectly conclude that there is no correlation between modulus and density. Rather than the magnitude of the modulus and density, one should compare at each particular composition the per-

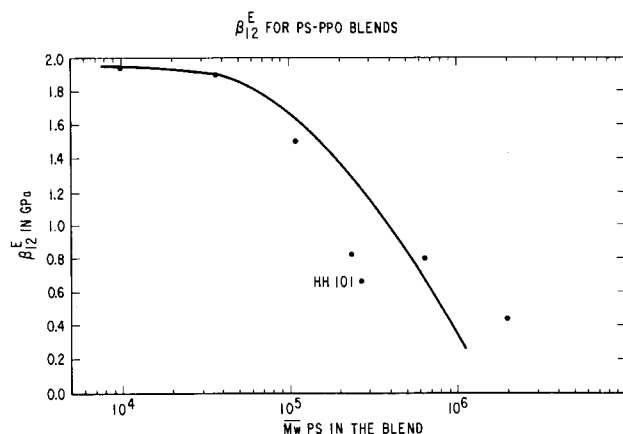


Fig. 2 Dependence of the interaction term,  $\beta_{12}^E$ , upon the weight average molecular weight of PS in the blend.

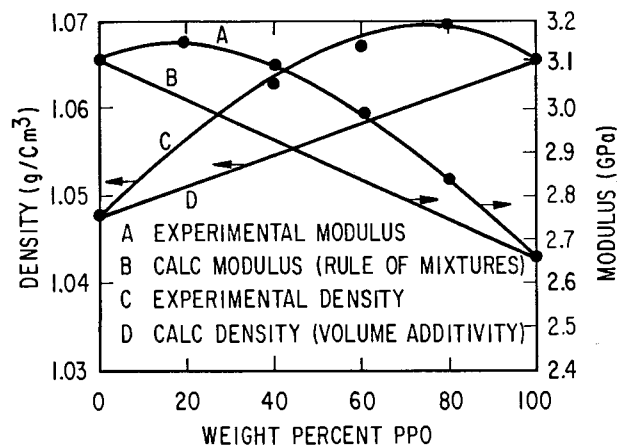


Fig. 3 Dependence of modulus and density upon composition.

cent increase in density and modulus over that which would be calculated assuming additivity of the homopolymer values. The additivity relationships for density and modulus respectively are:

$$\frac{1}{\rho_{blend}} = \frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} \quad (5)$$

and

$$E_{blend} = E_1\phi_1 + E_2\phi_2 \quad (6)$$

The percent densification and percent excess modulus as a function of composition is depicted in Fig. 4. The excess modulus is defined as that portion that deviates from linearity; i.e.,

$$E_{Excess} = E_{blend} - (\chi_1 E_1 + \chi_2 E_2) \quad (7)$$

where  $\chi_1$  and  $\chi_2$  refer to the composition of PS and PPO, respectively. Figure 4 indicates that there is a good correlation between densification and the observed blend modulus, since the two curves can be made to almost coincide with an appropriate enlargement of the density scale or contraction of the modulus scale. Better agreement may be possible with higher precision measurements. The precision for modulus and density was approximately 3 and 0.2 percent, respectively.

Previously, it was noted that the packing density is the only equilibrium quantity that reveals enhancement behavior similar to that found for the modulus in "anti-plasticizer" systems. In view of the similarities glassy alloys show to these systems (modulus, density, and tensile strength increases above that expected by assuming additivity), it would be desirable to also correlate blend modulus with packing density. The packing density,

$$\rho^*_B = \frac{V_w}{V} \quad (8)$$

can be defined as the ratio of the van der Waals volume over the molar volume (12). The theoretically calculated  $V_w$  represents the volume occupied by the polymer molecule which is impenetrable to other molecules with normal thermal energies (12, 23). The packing density is then a type of measure of occupied volume fraction. Figure 5 verifies the strong correlation between blend packing density and modulus. Figure 6 is analogous to Fig. 4. Hence, it can be seen that percent densification

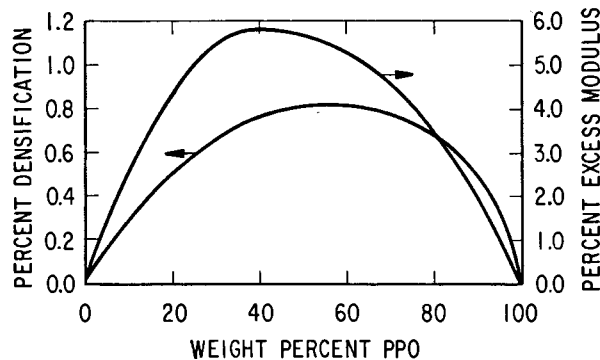


Fig. 4 Percent densification and percent excess modulus as a function of blend composition.

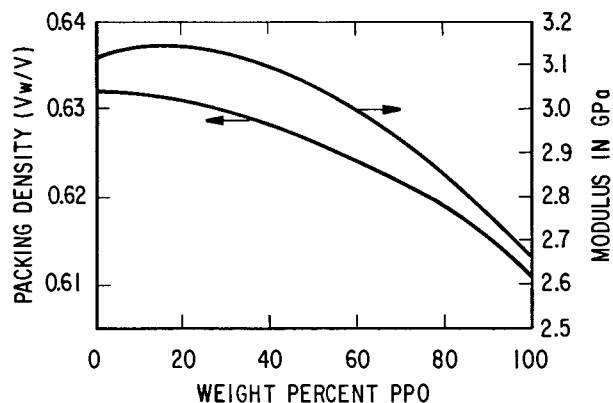


Fig. 5 Correlation between blend packing density and modulus.

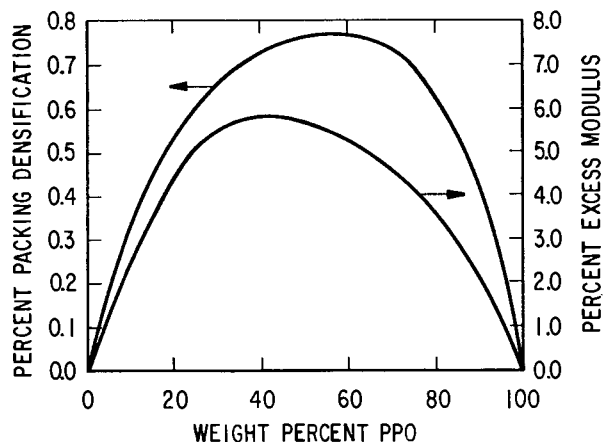


Fig. 6 Percent densification and percent excess modulus as a function of blend composition.

and the packing density,  $\rho^*_B$ , are the important parameters (rather than simply the magnitude of the experimentally measured density) in determining the modulus of the blend.

The cohesive energy density (CED) is another factor that influences the numerical magnitude of the modulus. It can be defined as the ratio of the heat of sublimation over the van der Waals volume (12), i.e.,

$$CED = \frac{H_s}{V_w} \quad (9)$$

These theoretically calculated fundamental parameters are measures of the lattice energy and molecular geometry, respectively. The modulus can be generalized and nondimensionalized in terms of these fundamental parameters via the following relationship:

$$E^* = \frac{E V_w}{H_s} \quad (10)$$

where  $E^*$  is termed the reduced modulus. The effect of molecular structure on the modulus of isotropic polymer glasses below the glass transition should be well represented by the reducing parameter  $H_s/V_w$ , indicating that the modulus reflects primarily the van der Waals interactions between molecules. The validity of this statement is verified in Fig. 7, where the reduced modulus,  $E^*$ , is presented as a function of the packing

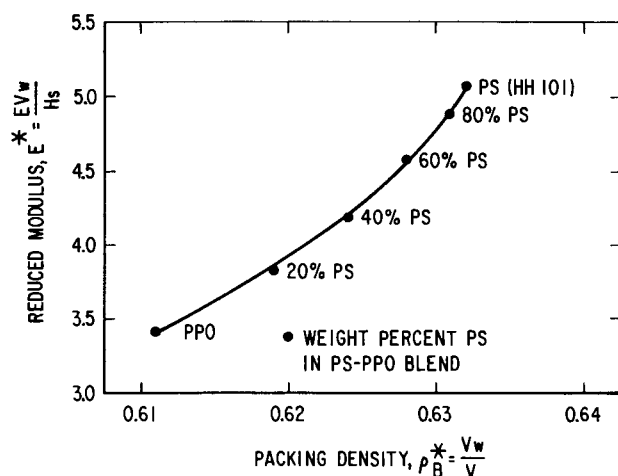


Fig. 7 Variation of the reduced modulus with blend packing density.

density,  $\rho_B^*$ . This relationship has additional utility in that one should be able to predict the modulus given that the packing density is known and  $H_s$  can be calculated from group increments. The predictive power should be best near absolute zero. Near this temperature, one does not have to cope with the blurring effects of secondary relaxations that influence the free volume.

The generalization and nondimensionalization of the modulus in terms of lattice energy,  $H_s$ , and molecule geometry,  $V_w$ , is not unique. The modulus can also be reduced using "lattice fluid" theory (24-28). In lattice fluid theory, the modulus can be reduced through  $P^*$ , the CED in the close-packed state, via

$$\bar{E} = \frac{E}{P^*} \quad (11)$$

where  $\bar{E}$  is reduced modulus.  $P^*$  is equivalent to the ratio of the energy required to create a "hole" in the lattice,  $\epsilon^*$ , over the close-packed volume,  $v^*$ :

$$P^* = \frac{\epsilon^*}{v^*} \quad (12)$$

In terms of experimentally accessible quantities,

$$P^* = T\alpha\bar{\rho}^2\beta \quad (13)$$

where  $\alpha$ ,  $\beta$ , and  $\bar{\rho}$  are the thermal expansion coefficient, isothermal compressibility, and the reduced density, respectively.

The reduced density,  $\bar{\rho}$ , is equivalent to  $\rho/\rho^*$ .  $\rho^*$  is the packing density at absolute zero. Therefore, the reduced density,  $\bar{\rho}$ , is a measure of occupied lattice volume. Now, a similar relationship as depicted in Fig. 7 can be generated and is illustrated in Fig. 8.

It should not be surprising that both Fig. 7 and Fig. 8 show similar trends, since both theories make use of lattice energy ( $H_s$  or  $P^*$ ) and molecule geometry or packing ( $\rho_B^*$  or  $\bar{\rho}$ ). It should be noted that while  $P^*$  is an experimentally accessible quantity,  $H_s$  is not. Both theories have some rather satisfying aspects. First, the reduced moduli,  $E^*$  and  $\bar{E}$  are higher for PS than for PPO, indicating that PS is a stiffer molecule. Second, the packing density,  $\rho_B^*$ , and the reduced density,  $\bar{\rho}$  are

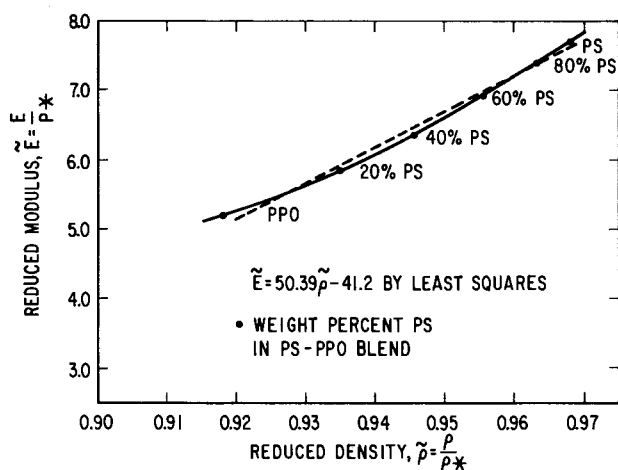


Fig. 8 Variation of the reduced modulus with reduced density of the blend.

less for PPO even though the experimental density of PPO is higher. These observations are in accordance with the empirical modulus results.

Without considerably more data, it is difficult to determine, at this point, whether the correlations depicted in Fig. 7 and Fig. 8 are universal for all glassy isotropic polymer blends. Evidence indicates that at least the  $E^*$  vs  $\rho_B^*$  correlation is universal for homopolymers (12). Universal or not, both theories allow one to predict the modulus of the blend at any composition if either the reduced density or the packing density for each homopolymer is known; i.e., for the PPO-PS system, any given  $\rho_B^*$  or  $\bar{\rho}$  immediately defines a unique blend composition and modulus. Without resorting to appropriate parameters that result in dimensionless groups, unique values cannot always be defined for polymer systems which exhibit excess moduli and densification. Figure 9 supports this point in that a particular density does not necessarily define a unique modulus or blend composition.

## CONCLUSION

It has been shown that composite equations cannot describe the modulus-compositional behavior of glassy alloys; however, a second order Simplex equation can be generated to model these empirical trends. Furthermore, there are strong indications that the interaction

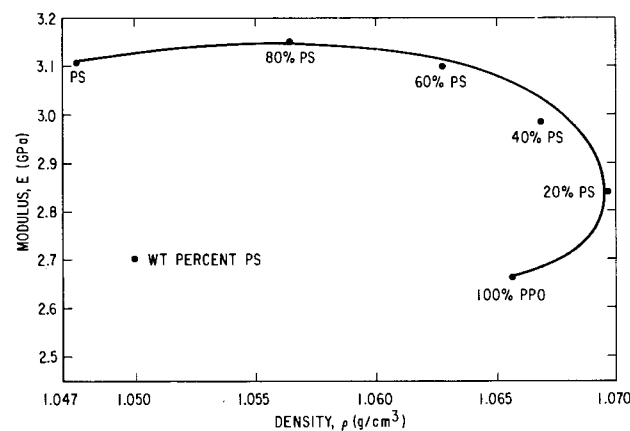


Fig. 9 Modulus and density as a function blend composition.

term,  $\beta_{12}^E$ , can be a useful gauge for compatibility and level of compatibility. Finally, it was found that the packing density,  $\rho^*$ , reduced density,  $\tilde{\rho}$ , and the CED, either  $H_s/V_w$  or  $P^*$ , are useful parameters for understanding the moduli of isotropic glassy polymer blends.

#### ACKNOWLEDGMENT

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