



Prediction of Phase Stability of Hydrogen Bonded Polymer Mixtures by Lattice Fluid Theory Approach

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Lattice fluid theory for hydrogen bonded fluid mixtures has been extended to predict phase stability and miscibility of hydrogen bonded polymer mixtures. Miscibility regions and spinodal curves for mixtures of ethylene vinyl phenol copolymer (PE-co-PVPh) with Poly Ethylene Oxide (PEO), Poly Vinyl Acetate (PVAc) and Poly Caprolactone (PCL) have been presented. The effect of change in the number of proton donor and proton acceptor functional groups on compatibilizing polymer mixtures and polymer miscibility has been considered.

INTRODUCTION

In many polymer mixtures, interactions between polymer chains are due to dispersion forces. It is well known that for these interactions, Gibbs free energy of mixing is usually positive because the combinatorial entropy contribution for mixing of high molecular weight polymers is negligible and the interaction parameter between the constituents of a polymer mixture is generally positive. Occurrence of a miscible mixture is concluded when specific interactions such as hydrogen bonding exist between the molecules. In such a case, the noncombinatorial entropic contribution which is associated with macromolecular interactions and related to their orientations would have a large positive value and, therefore, makes Gibbs free energy of mixture negative. When proton donor or acceptor functional groups exist in polymer chains, hydrogen bonding may occur between them. For example, polymers which contain amide, urethane or aromatic hydroxyl groups can produce hydrogen bonds with other chains which have proton acceptor functional groups.

In general, when the strong repulsion forces do not exist among components of a polymer mixture, and

the mixture is homogeneous in a visual macroscopic sense, the components are called compatible [1]. As an accepted rule, polymer compatibility has an important effect in polymer miscibility. For example, it is observed experimentally that mixture of Poly Styrene (PS) and Poly Methyl Methacrylate (PMMA) is immiscible [2]. However, PS can be copolymerized with Poly Vinyl Phenol (PVPh) to produce a miscible mixture with PMMA due to existence of hydroxyl functional groups.

The hydroxyl functional groups in PVPh can play the role of proton donor for the oxygen atom in PMMA chain which acts as a proton acceptor. Such specific interactions between chains are called hydrogen bonding. Now the question is how the number of necessary hydrogen bonds which can change an immiscible mixture to a miscible one can be predicted and what fraction of PVPh is necessary to be incorporated into PE in order to make it miscible with Poly Ethylene Oxide (PEO) ?

Many attempts have been made to predict the thermodynamic properties and the phase stability of hydrogen bonded polymer mixtures. Painter et al. [3] adopted the well known Flory-Huggins model for including the hydrogen bonding contribution in polymer miscibility, where an additional term was employed in Flory-Huggins Gibbs free energy expression of mixing that takes into account the effect of hydrogen bonding. To predict the distribution of hydrogen bonded chains in the mixture, they used the concept of association and equilibrium constants which were determined by spectroscopic measurements. In their initial model,

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they assumed that the size of a repeating unit of polymer chains was equal to an interacting unit. In their next model [4], the latter assumption was no longer necessary. Also, associating complexes which are formed through hydrogen bonding were considered as linear chains. Each of these associated complexes were independent and distinguishable. This was used in simulating the phase behavior of a number of polymer mixtures such as Poly Vinyl Phenol (PVPh) and polyacrylates.

The model of Painter et al. properly predicted the Upper and Lower Critical Solution Temperature (UCST and LCST) behavior of mixtures. Nevertheless, the effect of mixture compressibility or the free volume effect on polymer miscibility was not included. After these models, Graf et al. presented a new model [5] which utilized the Sanchez and Lacombe [6-8] lattice fluid theory of polymer mixtures. The equilibrium constants for predicting the distribution of hydrogen bonded chains were also used and through deriving a relation for the partition function of the mixture, Gibbs free energy of mixing was calculated. The final relation had three contributions. The first contribution was Flory-Huggins Gibbs free energy. The second contribution was due to hydrogen bonding changes upon mixing in absence of covalent bonds among polymer chain segments. The third contribution was a necessary correction term.

The effect of free volume or mixture compressibility was considered by Graf, et al. [5] in a new molecular theory for hydrogen bonded polymer mixtures which is based on the equation of state approach. They assumed some vacant sites in the lattice which played the role of free volume in the mixture. Thus, the effect of free volume on phase stability of mixture can be introduced in Gibbs free energy of mixing as a pressure-volume term. This model could predict the LCST behavior of hydrogen bonded polymer mixtures such as poly vinyl phenol and poly butyl methacrylate.

On the other hand, Panayiotou and Sanchez presented an excellent model [9] for hydrogen bonding in fluids, with equation of state approach. This model divides the intermolecular forces into two contributions which are physical (dispersion) and chemical (hydrogen bonding) forces. The physical forces are calculated based on the lattice theory of fluid mixtures and the chemical interactions are taken into account through calculating the number of hydrogen bonds among hydrogen bonding donor and acceptor groups.

In this work, conditions which are required for phase separation of polymer mixtures are first introduced. Then, Panayiotou and Sanchez [8] lattice theory for hydrogen bonded fluid mixtures is extended to include the hydrogen bonded polymer mixtures through introducing an additional term to the chemical potential expression and, consequently, the phase sep-

aration condition is obtained. This equation is the first derivative of the chemical potential of k th component in the mixture. Applying the equations derived in this work to hydrogen bonded polymer mixtures resulted in prediction of miscibility regions or spinodal curves for mixtures of ethylene vinyl phenol copolymer (PE-co -PVPh) with PVAc, poly caprolatone (PCL) and Poly Ethylene Oxide (PEO). The results of calculations show that the proposed equations are capable of correctly predicting the phase behavior of these mixtures.

THEORY

The spinodal curve separates the miscible or stable phase from the metastable phase, the equation defining this curve is called the spinodal equation. To derive an spinodal equation, different variables must be recognized which are effective on phase stability. There are m types of proton donor and n types of proton acceptor functional groups in the mixture. The number of hydrogen bonds among the i th proton donor and j th proton acceptor functional groups is shown by N_{ij} . Where i represents the counter of m ($i = 1$ to m) and j represents the counter of n ($j = 1$ to n).

The spinodal can be written as the determinant of a square matrix [10]. The elements of this matrix are the partial derivative of the total Gibbs free energy of the system with respect to $t - 1$ composition variables (for a t -component system) and the $mn + 1$ order parameter, i.e., the set of $\{N_{ij}\}$ plus ρ , which is the density of the mixture. This is because there are m donors and n acceptors plus one density variable. Based on the number of order parameters, the size of the determinant is equal to $t + mn$. The second partial derivatives of the total Gibbs free energy of the mixture appearing in this determinant are, with respect to the two by two combination of the $t - 1$, independent composition variables, the density variable and the mn pair number variables.

In the binary mixture considered here $t = 2$ (two components), $m = 1$ due to one type of proton donor, e.g., hydroxyl functional group and $n = 2$ since there are two types of proton acceptor, e.g., hydroxyl group and oxygen group. Thus, the spinodal matrix can be written as follows:

$$\begin{vmatrix} \left(\frac{\partial^2 G}{\partial \bar{\rho} \partial \varphi_1}\right)_{T,P,[N_{ij}]} & \left(\frac{\partial^2 G}{\partial \bar{\rho}^2}\right)_{T,P,\varphi_1,[N_{ij}]} \\ \left(\frac{\partial^2 G}{\partial N_{12} \partial \varphi_1}\right)_{T,P,\bar{\rho},[N_{ij}-N_{12}]} & \left(\frac{\partial^2 G}{\partial N_{12} \partial \bar{\rho}}\right)_{T,P,\varphi_1,[N_{ij}-N_{12}]} \\ \left(\frac{\partial^2 G}{\partial \varphi_1^2}\right)_{T,P,\bar{\rho},[N_{ij}]} & \left(\frac{\partial^2 G}{\partial \varphi_1 \partial \bar{\rho}}\right)_{T,P,[N_{ij}]} \\ \left(\frac{\partial^2 G}{\partial N_{11} \partial \varphi_1}\right)_{T,P,\bar{\rho},[N_{ij}-N_{11}]} & \left(\frac{\partial^2 G}{\partial N_{11} \partial \bar{\rho}}\right)_{T,P,\varphi_1,[N_{ij}-N_{11}]} \\ \left(\frac{\partial^2 G}{\partial \bar{\rho} \partial N_{11}}\right)_{T,P,\varphi_1,[N_{ij}-N_{11}]} & \left(\frac{\partial^2 G}{\partial \bar{\rho} \partial N_{12}}\right)_{T,P,\varphi_1,[N_{ij}-N_{12}]} \\ \left(\frac{\partial^2 G}{\partial N_{12} N_{11}}\right)_{T,P,\varphi_1,\bar{\rho}} & \left(\frac{\partial^2 G}{\partial N_{12}^2}\right)_{T,P,\varphi_1,\bar{\rho},[N_{ij}-N_{12}]} \\ \left(\frac{\partial^2 G}{\partial \varphi_1 \partial N_{11}}\right)_{T,P,\bar{\rho},[N_{ij}-N_{11}]} & \left(\frac{\partial^2 G}{\partial \varphi_1 \partial N_{12}}\right)_{T,P,\bar{\rho},[N_{ij}-N_{12}]} \\ \left(\frac{\partial^2 G}{\partial N_{11}^2}\right)_{T,P,\varphi_1,\bar{\rho},[N_{ij}-N_{11}]} & \left(\frac{\partial^2 G}{\partial N_{11} \partial N_{12}}\right)_{T,P,\varphi_1,\bar{\rho}} \end{vmatrix}$$

where φ_i is volume fraction and defined as:

$$\varphi_i = \frac{N_i r_i}{\sum N_i r_i}. \quad (1)$$

The other symbols are introduced in Nomenclature.

All elements of this matrix except the 1×1 terms are zero because in deriving Gibbs free energy relation for the mixture, the following minimization conditions are imposed:

$$\left(\frac{\partial G}{\partial \bar{p}}\right)_{T,P,[N_{ij}],[N_k]} = 0, \quad (2)$$

$$\left(\frac{\partial G}{\partial N_{ij}}\right)_{T,P,\bar{p},[N_k],[N_{gh}]} = 0. \quad (3)$$

Therefore, the spinodal is readily evaluated from the following relation:

$$\left(\frac{\partial^2 G}{\partial \varphi_1^2}\right)_{T,P,\bar{p},[N_{ij}]} = 0. \quad (4)$$

If in Equation 4, the chemical potential of component 1 is considered, the first derivative of the chemical potential will be used. The chemical potential of the k th component, μ_k , in the mixture can be divided into two parts:

$$\mu_k = \left(\frac{\partial G}{\partial N_k}\right)_{T,P,[N_j],[N_{ij}]} = \mu_{LF,k} + \mu_{H,k}, \quad (5)$$

where $\mu_{LF,k}$ is the lattice fluid contribution and $\mu_{H,k}$ is the hydrogen bonding contribution [9]. Therefore, the unstable phase region can be obtained by the following relation:

$$\frac{\partial \mu_k}{\partial \varphi_k} = \frac{\partial \mu_{LF,k}}{\partial \varphi_k} + \frac{\partial \mu_{H,k}}{\partial \varphi_k} = 0. \quad (6)$$

The first term of Equation 6 was calculated previously by Sanchez and Lacombe [8] and it is given in Appendix A.

Here, an expression is provided for the second term of Equation 6 from hydrogen bonding contribution of chemical potential $\mu_{H,1}$ in a mixture that one component can self associate and the other can only associate with the self associative component as proposed by Panayiotou et al. [9] in the following form:

$$\frac{\mu_{H,1}}{RT} = r_1 \nu_H - d \ln\left(\frac{dx_1}{dx_1 - r \nu_H}\right) - d \ln\left(\frac{dx_1}{dx_1 - r \nu_{11}}\right), \quad (7)$$

where x_1 is the mole fraction of component 1 and is defined as:

$$x_1 = \frac{N_1}{N}, \quad (8)$$

and ν_{ij} is obtained from the following relation:

$$\nu_{ij} = N_{ij} / \sum N_i r_i, \quad (9)$$

where d is the number of proton donors or hydroxyl functional groups per molecule and $\nu_H = \sum \sum \nu_{ij}$.

At this stage, Equation 8 is differentiated with respect to φ_1 and the following equation is obtained:

$$\left[\frac{d(\mu_{H,1}/kT)}{d\varphi_1}\right]_{T,P,\varphi_2} = 2[r + \varphi_1(\partial r/\partial \varphi_1)]/r\varphi_1 - \xi_H - \xi_{11}, \quad (10)$$

where parameters ξ_H and ξ_{11} are defined as:

$$\xi_H = \frac{d[r + \varphi_1(\partial r/\partial \varphi_1)] - r_1 \nu_H (\partial r/\partial \varphi_1)}{rd\varphi_1 - rr_1 \nu_H}, \quad (11)$$

$$\xi_{11} = \frac{d[r + \varphi_1(\partial r/\partial \varphi_1)] - r_1 \nu_{11} (\partial r/\partial \varphi_1)}{rd\varphi_1 - rr_1 \nu_{11}}. \quad (12)$$

As mentioned earlier, hydrogen bonding formation among polymer chains increases the tendency of components to miscibility. Equation 10 reflects the important effect of hydrogen bonding on phase stability conditions and will be used to obtain spinodal curves. The partial derivative term $(\partial r/\partial \varphi_1)$ appearing in Equations 11 and 12 can be derived from the relation $1/r = \varphi_1/r_1 + \varphi_2/r_2$ and becomes:

$$(\partial r/\partial \varphi_1) = \frac{-r^2(\nu_1^*/\nu_2^*)(1/r_1^0 - 1/r_2^0)}{[\varphi_1 + (\nu_1^*/\nu_2^*)\varphi_2]^2}, \quad (13)$$

where the superscript "0" refers to the values for the pure component.

CALCULATIONS

In a two component polymer mixture, two terms of Equation 6, $\partial \mu_{LF,1}/\partial \varphi_1$ and $\partial \mu_{H,1}/\partial \varphi_1$, are necessary for calculating the miscibility range. The following lattice fluid contribution $\partial \mu_{LF,1}/\partial \varphi_1$, is obtained by Sanchez and Lacombe [8] :

$$\left(\frac{\partial \mu_{LF,1}}{\partial \varphi_1}\right)_{T,P,\varphi_2} = [2r_1 \varphi_2 \left[\frac{1}{2} \left(\frac{1}{r_1 \varphi_1} + \frac{1}{r_2 \varphi_2}\right) - \bar{\rho} \left[X + \frac{1}{2} \Psi^2 \tilde{T} P^* \beta\right]\right]], \quad (14)$$

moreover, $\partial \mu_{H,1}/\partial \varphi_1$ is given in Equation 10. Adding Equations 14 and 10 yields:

$$\left(\frac{\partial \mu_1}{\partial \varphi_1}\right)_{T,P,\varphi_2} = [2r_1 \varphi_2 \left[\frac{1}{2} \left(\frac{1}{r_1 \varphi_1} + \frac{1}{r_2 \varphi_2}\right) - \bar{\rho} \left[X + \frac{1}{2} \Psi^2 \tilde{T} P^* \beta\right]\right] + 2[r + \varphi_1(\partial r/\partial \varphi_1)]/(r\varphi_1) - \xi_H - \xi_{11}, \quad (15)$$

where ξ_H , ξ_{11} are given by Equations 11 and 12 and the expressions of the other terms are provided in Appendix A.

In two component systems considered in this work, the hydroxyl functional group of PVPh can act both as a proton donor and a proton acceptor. Therefore, two types of hydrogen bonds can be assumed for a mixture of PVPh-co-PE with PEO, one between PVPh repeating units and the other between PVPh repeating units and PEO. The fraction of similar and nonsimilar hydrogen bonded repeating units are assigned by ν_{11} and ν_{12} , respectively.

Through minimizing Gibbs free energy of mixture with respect to the number of hydrogen bonds the necessary equations for calculating ν_{11} and ν_{12} are obtained. These equations are given in Appendix B. To calculate ξ_H and ξ_{11} of Equations 11 and 12, ν_H is required which represents the fraction of hydrogen bonds in the mixture and is defined as $\nu_H = \nu_{11} + \nu_{12}$. As seen from Equations A5 to A8 in Appendix B, ν_{11} and ν_{12} are expressed in terms of G_{11} and G_{12} , therefore, to proceed with calculations, G_{11} and G_{12} are needed. Sanchez and Panayiotou [9] have proposed that the hydrogen bonding characteristic values, such as Gibbs free energy changes upon hydrogen bonding formation, is set equal to known values of simple molecules such as 1-alkanols. It is clear that this approximation can cause a considerable error in spinodal calculations. A small molecule is more capable of having random orientation and free motion than a functional group which has limited orientations due to covalent bonding in a polymer chain. Furthermore, the steric hindrance effect of neighboring repeating units in polymer chains can cause more limitations. Thus, no similarity can be found between hydrogen bond formation in the case of small molecules and polymer chains and the suggestion of Sanchez and Panayiotou for equality of Gibbs free energy changes is not accurate.

In the present work, this problem is overcome by applying the concept of association which assumes equilibrium reactions for hydrogen bonding formation between the polymer chains. According to this assumptions, a unique equilibrium constant can characterize an equilibrium reaction regardless of the hydrogen bonded chain length. For example, hydrogen bonding formation for a self associated polymer according to the following reaction:



can be characterized by k_{ii} . x and y are the number of functional groups which have formed hydrogen bonded chains and k_{ii} is independent of x and y . Using this assumption, G_{ij} can be calculated for hydrogen bonding formation from the following equation [11]:

$$G_{ij} = -RT \ln(k_{ij}). \quad (17)$$

The equilibrium constants can be determined by infrared spectroscopic measurements. Also for the variation of equilibrium constant k_{ij} with temperature the Vant Hoff equation is used as [12]:

$$k_{ij} = k_{ij}^{\circ} \exp\left[-\frac{\Delta h}{R}(1/T - 1/T^{\circ})\right], \quad (18)$$

where k_{ij}° is the equilibrium constant at T° and its values for mixtures of PVPh and some different polymers have been presented in Table 1.

RESULTS AND DISCUSSION

Using Equation 15 the chemical potential derivative with respect to volume fraction for the mixture of PEO and PE-co-PVPh (7% by weight PVPh in copolymer) is obtained. Figure 1 shows the plot of chemical potential derivative versus volume fraction of PEO at temperatures 320 K and 400 K. To consider the phase stability in the polymer mixtures, the plots of chemical potential derivative versus volume fraction of a component in the mixture at different temperatures are needed. Three kinds of plot may be expected according to the theory of phase stability [13]. As seen from Figure 1 for 400 K, the chemical potential intersects the zero axis at 0.16 and 0.90 volume fractions of PEO. According to the phase stability theory, this behavior means that a new phase appears in this system in the region of $0.16 < \varphi_{PEO} < 0.90$ in which the derivative is negative.

Similar plots have been obtained for the mixtures of PE-co-PVPh with PCL and PE-co-PVPh with PVAc, which are not presented here. In Figures

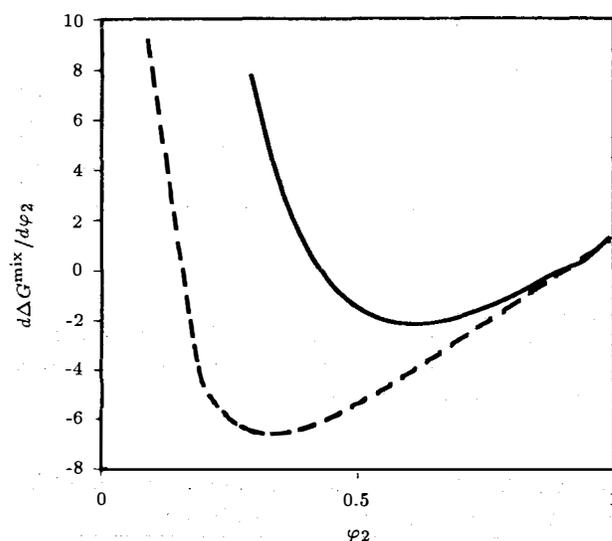


Figure 1. First derivative of chemical potential for PEO and PE-co-PVPh mixture at 320 K (solid curve) and 400 K (dashed curve). Weight percent of PVPh is 7% and degree of polymerization is 50.

Table 1. Hydrogen bonding parameters for mixture of PVPh and different polymers.

Polymer	Equilibrium Constant at 25°C	Enthalpy of Hydrogen Bond Formation
PVAc [5]	58.7	-3.8 kcal/mol
PEO [14]	62.8	-5.4
PCL [15]	66.2	-4.3

2 to 4, the spinodal curves are presented for the mixtures of PEO, PCL and PVAc with PE-co-PVPh, respectively. It is worth noting that to obtain each of these curves for a mixture, the intersection points for various temperatures, as is seen in Figure 1, are needed. Obtaining these points requires lengthy and complicated calculations.

Figures 2 to 4 demonstrate the existence of LCST in all the mixtures. These are also presented in Table 2. LCST is an important characteristic for hydrogen bonded mixtures. It is the minimum temperature at above which a stable phase cannot exist and the mixture splits into two phases. For hydrogen bonding, the physical meaning of this phenomena is that for

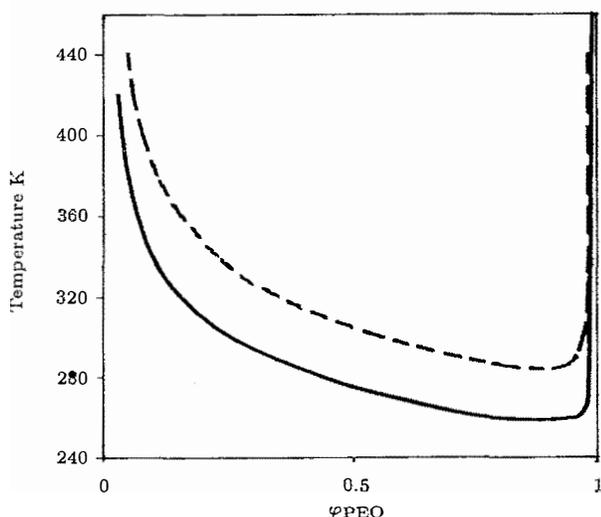


Figure 2. Spinodal curves for PEO and PE-co-PVPh mixture for 3 (solid curve) and 7 (dashed curve) weight percent of PVPh in copolymer. Degree of polymerization is 500 for both components.

Table 2. LCSTs for mixtures of PEO, PVAc and PCL with 3% by weight PVPh in (PE-co-PVPh).

Mixture	LCST(k)
PE-co-PVPh and PEO	249
PE-co-PVPh and PVAc	300
PE-co-PVPh and PCL	291

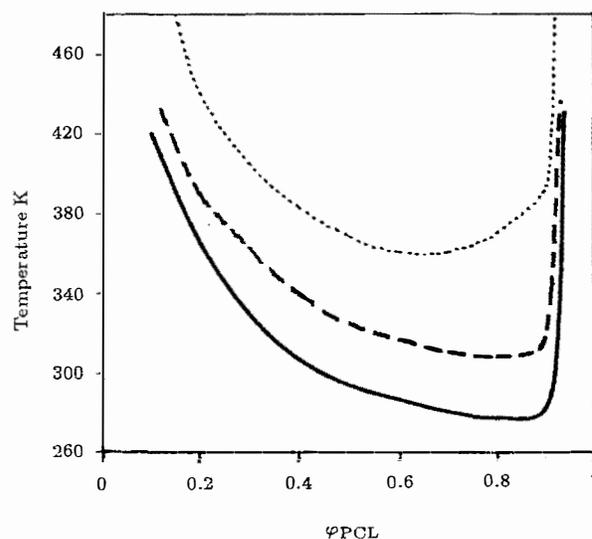


Figure 3. Spinodal curves for PCL and PE-co-PVPh mixture at various weight percents of PVPh (solid curve 3%, heavy dashed curve 5% and light dashed curve 7%) in copolymer. Degree of polymerization is 500 for both components.

a specified hydrogen bonded polymer mixture with constant composition, increasing temperature causes higher mobility of polymer chains and decreases the mixture viscosity. This leads to break of some of the hydrogen bonds and, consequently, decreases the enthalpy term with a minus sign in the following well known thermodynamic relation:

$$\Delta G = \Delta H - T\Delta S. \quad (19)$$

Thus, an increase in the Gibbs free energy of mixing seems to result in separation of the mixture into two phases. Moreover, the effect of varying the number of hydrogen bonds due to an increase in the percentage of hydroxyl groups in PE-co-PVPh on the miscibility region area is shown in Figures 2 to 4.

In Figure 5, the variation of ν_{11} , ν_{12} and ν_H with composition are shown for a mixture of PEO and PE-co-PVPh at temperature 320 K. As seen from this figure, for a degree of polymerization equal to 50 and 7% by weight PVPh in copolymer, ν_H has a maximum of about 0.2 (volume fraction of PE-co-PVPh). This means that by increasing the volume fraction of the

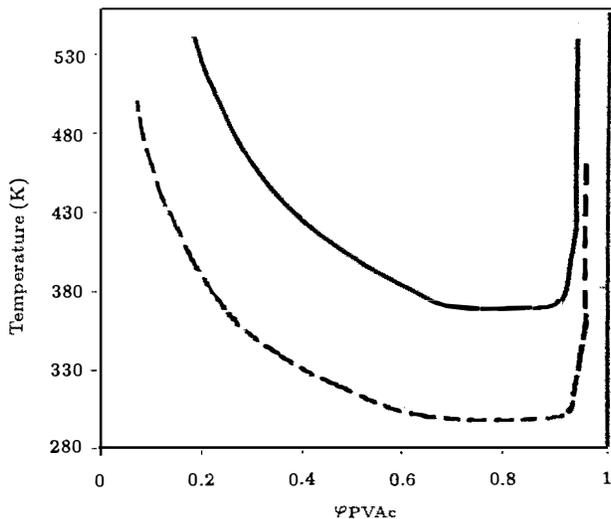


Figure 4. Spinodal curves for PVAc and PVAc-co-PVPh mixture at various weight percents of PVPh (dashed curve 3% and solid curve 9%) in copolymer. Degree of polymerization is 500 for both components.

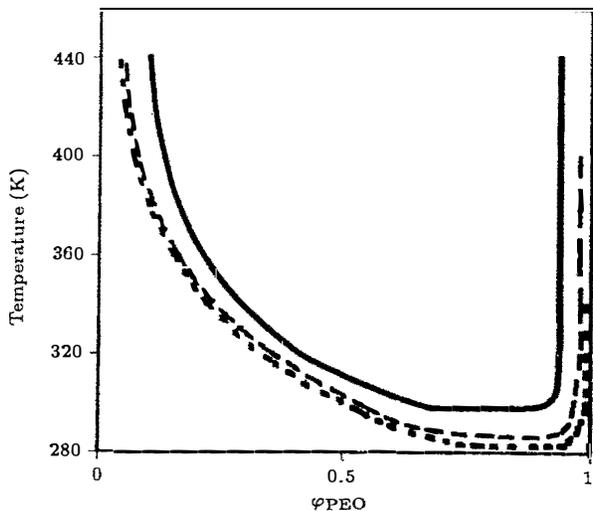


Figure 5. Hydrogen bond fractions for PEO and PE-co-PVPh mixture at 320 K.

copolymer, the number of total hydrogen bonds at first increases and reaches a maximum, since the number of proton donor functional groups (hydroxyl groups) has correspondingly increased. However, with further increase in the PE-co-PVPh volume fraction a tendency is observed for ν_H . This behavior is acceptable, since by increasing the volume fraction of copolymer, the number of proton acceptor functional groups decreases simultaneously.

The degree of polymerization has an important role in phase stability of polymer solutions. For simplicity, only the monodispersed polymer chains have been considered. In Figure 6, the spinodal curve is plotted for degree of polymerization varying from 50 to 50000 for both components. This figure shows

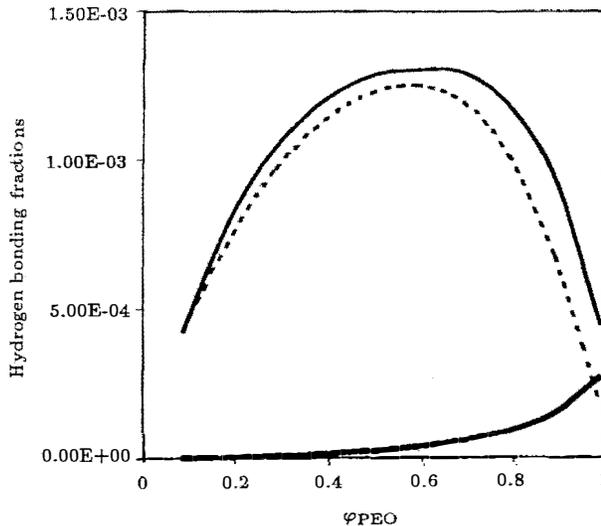


Figure 6. Effect of degree of polymerization on phase stability of PEO and PE-co-PVPh mixture ($M_w = 50000$ heavy dashed curve, $M_w = 500$ light dashed curve and $M_w = 50$ solid curve). Weight percent of PVPh in copolymer is equal to 7%.

that increasing the degree of polymerization leads to polymer miscibility decrease. For molecular weights higher than 500 and temperatures above 340 K, the lower miscibility limit of copolymer in PEO approaches zero. The reason for this behavior is that at low volume fractions of PE-co-PVPh the number of favorable hydrogen bonds for miscibility has not still reached a considerable value.

CONCLUSION

Phase behavior of polymer mixtures in the presence of strong specific intermolecular interactions such as hydrogen bonding, which can produce associated complexes, differs widely from usual cases where dispersion forces dominate the problem. A new spinodal equation based on lattice fluid theory was presented and used in phase stability prediction. The spinodal curves are obtained for three different hydrogen bonded polymer mixtures.

The results indicated that LCST appearance can be well predicted for polymer mixtures. Unfortunately, no experimental data was available to assess the accuracy of the predicted LCSTs. However, considering the quantitative behavior of the mixtures in the spinodal curves confirms the capability of the theory and the derived equations.

A procedure for calculating the number of hydrogen bonds which is needed to produce a miscible mixture from two incompatible polymers was suggested. The number of hydrogen bonds can indicate the minimum percentage of a polymer which is required in the process of copolymerization. This point is very important in compatibilizing polymer mixtures to

produce homogeneous material with desired physical properties.

NOMENCLATURE

d	number of proton donor groups per polymer chain
E	internal energy
G	Gibbs free energy
h	enthalpy change of hydrogen bonding formation
k	Boltzman constant
M	degree of polymerization
N	number of molecules
N_{ij}	number of hydrogen bonds
k_{ij}	equilibrium constant
P	pressure
R	gas constant
r	number of segments
S	entropy
T	temperature
x	mole fraction
ρ	density
ν	ratio of closed packed lattice cell volume of components
φ	volume fraction
μ	chemical potential

Indexes

i	i th component
j	j th component

Superscripts

\sim	reduced variables
\circ	pure component state
$*$	closed packed state

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APPENDIX A

In the text it is mentioned that the lattice fluid contribution of chemical potential derivative with respect to volume fraction, which arises from physical forces, was obtained previously by Sanchez and Lacombe [8]. The form of this equation is as follows:

$$\frac{d(\mu_{L,F,k}/kT)}{d\varphi_k} = 2r_1\varphi_2\left[\frac{1}{2}\left[\frac{1}{r_1\varphi_1} + \frac{1}{r_2\varphi_2}\right] - \bar{\rho}\left[X + \frac{1}{2}\Psi^2\tilde{T}P^*\beta\right]\right], \quad (A1)$$

where Ψ is a dimensionless function defined by:

$$\bar{\rho}\left[\nu(1/\tilde{T}_1 - 1/\tilde{T}_2) + (\varphi_1^2 - \nu\varphi_2^2)X_1\right] - \nu(1/r_1^\circ - 1/r_2^\circ) + \frac{\bar{P}\bar{\nu}}{\tilde{T}}(\nu - 1)(\varphi_1 + \nu\varphi_2)/(\varphi_1 + \nu\varphi_2), \quad (A2)$$

and X_1 is as follows:

$$X_1 = \Delta P^*\nu_1^*/kT, \quad (A3)$$

where parameter ν in the above relations is the ratio of closed packed lattice volumes. Finally, β is the isothermal compressibility of the mixture and is obtained from

the following relation:

$$\beta = \frac{\tilde{\nu}}{[\frac{1}{\tilde{\nu}-1} + \frac{1}{r} - \frac{2}{\tilde{\nu}T}]P^*\tilde{T}}. \quad (\text{A4})$$

APPENDIX B

The necessary equations for calculating the fraction of hydrogen bonds in the mixture are as follows:

$$r\nu_{11} = [2dx_1 + \alpha_{11} - r\nu_{12} - [(2dx_1 + \alpha_{11} - r\nu_{12})^2 - 4dx_1(dx_1 - r\nu_{12})]^{1/2}]/2, \quad (\text{A5})$$

and:

$$r\nu_{12} = [dx_1 + ax_2 + \alpha_{12} - r\nu_{11} - [(dx_1 + ax_2 + \alpha_{12} - r\nu_{11})^2 - 4ax_2(dx_1 - r\nu_{11})]^{1/2}]/2, \quad (\text{A6})$$

where a is the number of repeating unit acceptors in a polymer chain and α_{11} and α_{12} are obtained as follows:

$$\alpha_{11} = r\tilde{\nu} \exp(G_{11}^\circ/RT), \quad (\text{A7})$$

$$\alpha_{12} = r\tilde{\nu} \exp(G_{12}^\circ/RT). \quad (\text{A8})$$

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