



## **CHEM303 PHYSICAL CHEMISTRY**

### Thermodynamic Aspects of Polymer Blends

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## Introduction

Polymers are formed by chains of groups of atoms; they can be synthetic or natural. All the polymers are the creation of specific macromolecules, these are the small molecular building blocks. Biopolymers are macromolecules which naturally occurred substances we can give example a proteins or polysaccharides in a life form. Synthetic polymers invented in early 1900s after 1960s humankind used these molecular chains with every sector: toys, computers, pipes, cables and so on.

We can classify plastics as three main topics, first one is Thermoplastics. In thermoplastics instantly softens when it's heated because of bonds in between molecules are weak. This specific condition makes it very useful for wide scenarios. Second is Thermosets, thermosets are cross-linked polymer chains which solidifies permanently when heated. These are more stronger and more durable type of polymer. Last one is elastomers; elastomers are rubbery type of polymer they are elastic which after stretched or squeezed it returns its original shape.

Thermodynamics are basically energy relationship between work, heat and temperature in a closed system. While we use polymer and polymer blends, we need to know the first, second and third law of the thermodynamics. The first law is the thermodynamics states conservation of energy in a closed system, if system is closed total energy of system is constant. We can define it with formula.

$$dU = dW + dQ = 0$$

In this formula Q is thermal energy content change while W is the work by or done the system. The second law of thermodynamics is the principle of entropy increase. In a closed system energy flows from higher to lower. System wants to move to more uniform energy states. Entropy is randomness, so entropy never decreases in closed system.

$$dS = dQ/T > 0$$

In third law of thermodynamics determinates the degree of disorder and randomness in closed system, we can also say as the absolute temperature approaches to zero equilibrium of entropy tends toward zero.

At some point polymers did not have enough property, we needed to use it for more specific, different areas. Polymer blends came through from this idea, they contain at least two or more polymer and different specifications. Nowadays improving mechanical properties of polymers in specific classifications. First one toughness, rigidity for a long-time industry blends polymers to get harder, tougher more durable to use in more areas. Dimensional stability is important to make solid blend. Especially durable at higher temperatures for longest time possible. Third one is water absorptivity. Some of the polymers are weak against water industry tries to blend one into another to create more stable also water-resistant blends. Environmental stress is also highly demand property of polymers. Just like rubber, industry tries to make stronger but in a same time elastic polymers. Creating a polymer blend is seems easy to make but the problem with that some polymers are not miscible. Polymer systems have three levels of predictions. Complex mixtures like copolymers needs much more effort to find partial miscibility. Polymer blends performance depends on components of the polymers and their molecular arranging in space. For example, imagine polymers with non-polar hydrocarbon chains normally it should be mixed without any problem. But they are not. We can find the problem if we dig into thermodynamics. With the help of second law of thermodynamics we can create a condition for miscible mixture from two polymers.

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

$\Delta G_{\text{mix}}$  (free mixing energy) should be less than zero, enthalpy of mixing is  $\Delta H_{\text{mix}}$ . To make  $\Delta G_{\text{mix}}$  to lower than zero we can use  $\Delta H_{\text{mix}}$  to make it negative. These conditions can be adjusted in between polymers in a mixture. We can adjust it by hydrogen bonds or dipole-dipole interactions.

### **FSH (Flory-huggins lattice theory of polymer solutions) model**

Thermodynamics of polymers investigated in 1940s by Paul Flory and Maurice Huggins. They create a table called two-dimensional lattice table. Huggins obtained

entropy of mixing using this theory. FSH only contain qualitative information about polymer blends. In FSH model X is the interaction parameter is discovered to be closely linked to the structure of the polymer mix. This independence can be caused by a variety of factors, the most common of this is the size and form difference between the repeating units in the system. Experiments show the location and structure of miscibility gaps are sensitive to changes in the number of closest interactions, which may be related to the repeating units' Van der Waals surface areas. Calculations using the FHS equation for  $\Delta G$  or expanded variants show that polymer blends are not in thermodynamic equilibrium in their processed state. In one of two methods, such blends likely strive to reach equilibrium through time. First, a partly miscible blend's Gibbs energy can be reduced by further phase separation into a lower mutual solubility state. However, if additional measures are applied, the reverse effect of phase separation towards increased. Help of resolve will occur in immiscible relatively quasi-binary mixtures. We used the word "thermodynamic aging" to describe the phenomena, which is distinct from common nature of aging such as physical and chemical aging.

Equation 1

$$\Delta G/NRT = \sum (\phi_{1i}/m_{1i}) \ln \phi_{1i} + \sum (\phi_{2j}/m_{2j}) \ln \phi_{2j} + \Gamma$$

$\sum n_{1i}$  moles of  $P_1$  while  $\sum n_{2j}$  moles of  $P_2$ .  $RT$  used as normal meaning these calculations covers in each two polymers. Number of basic volume units (BVU) occupied by  $l$  chain in component of  $k$  is  $m_{kl}$ . In this model,  $\phi_{kl}$  is represents the component  $l$  volume fraction in constituent  $k$ . To allow improvements, utilize the interaction function  $r$ . In the majority of situations, this entails a more or less complicated reliance on the overall:  $P_1$  and  $P_2$  volume fractions

Equation 2

$$\phi_{kl} = n_{kl} m_{kl} / N$$

Equation 3

$$\phi_1 = \sum \phi_{1i} = 1 - \phi_2; \phi_2 = \sum \phi_{2j}$$

Equation 4

$$\phi_k m_{wk} = \sum \phi_{kf} m_{kf}; \phi_k m_{wk} m_{zk} = \sum \phi_{kf} m_{kf}$$

Equation 5

$$\Gamma = \chi \phi_1 \phi_2; \chi = \chi_s + h/T$$

Equation 4 defines the basic volume units of P<sub>1</sub> and P<sub>2</sub>. In this equation enthalpic and entropic references as  $\chi_s$  and  $h$ . Numerical methods for calculating binary and quasi-binary phase diagrams for blends have been devised.

## Result and discussion

Polymer blends are strongly attached to thermodynamics, without the help of thermodynamics chemists and industry can not create most of the blends. In this part I want to discuss about results and graphs that I got from equations and articles

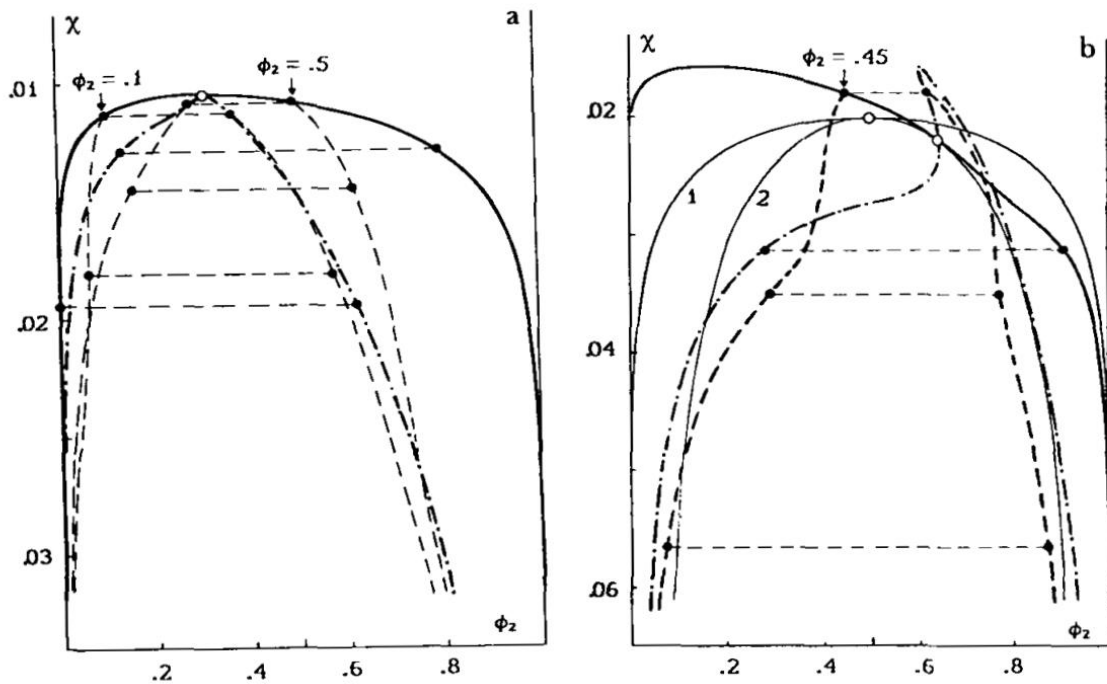


Figure 1: Quasi-binary  $\chi(\phi_2)$  phase diagrams calculated with equations.

For  $\Sigma_{n1} = \Sigma_{n2} = 2$ ,  $\Sigma_{w1}$  and  $\Sigma_{w2} = 2$  coexistence curves shown for  $\phi_2=0.1$  and  $0.5$ .  $\Sigma_{w1}=1.5$ . and heavy curves  $\Sigma_{w2} = 5$  coexistence curves shown  $\phi_2=0.5$  and light curves cpc or  $\Sigma_{w2} = 1.5$

In Figure 1 we saw graph a and graph b determined by equations from introduction part it show us quasi-binary phase diagrams of calculated values. If the  $\Sigma_w$  results differ, the critical point moves away from the maximum and toward the plane of the polymeric component with the higher 5, number. Once the parameters of  $m_w$ ,  $\Sigma_n$ , and  $\Sigma_w$  were fixed, phase diagrams generated using four-component and continuous mmd's look almost identical, demonstrating relative insensitivity to the number of components of a constituent.

## Conclusion

In the end we learned about polymers, polymer blends, thermodynamics and relationship between thermodynamics and polymer blends. To summarise polymers are combination of one or more substances these substances are called as macromolecules. In industry most used polymers are plastics we can classify them as thermoplastics, elastomers and thermosets. Thermodynamics are energy relationship between work, heat and temperature in a closed system. We use thermodynamics in order to create polymer blends. Polymer blends are mixture of more than one polymer it contains different specifications than single polymer for example one of the polymers has elastic feature other one can withstand high temperatures if we mix them together it can be elastic and resistant to high temperatures polymer blend. Sometimes we could not mix polymers easily even if they look pretty similar. To get rid of this problem we use thermodynamics to create new blends that can't be created in natural ways. We mostly 2<sup>nd</sup> law of thermodynamic (principle of entropy) to blend them together. FSH (lattice theory) is useful way to guess polymer blends. Thermodynamics of polymers investigated by Flory and Huggins and they created a model with idea of lattice this model helps us with qualitative approach of polymer blends. In this article I tried to explain about information about what they did and explained effect of thermodynamics on polymer blends.

## Resources

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