STUDY OF GENISTEIN /EPOXIDIZED NATURAL RUBBER (ENR) BLENDS AND ITS APPLICATION FOR POLY (VINYL CHLORIDE) (PVC) PLASTICIZATION

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STUDY OF GENISTEIN / EPOXIDIZED NATURAL RUBBER (ENR) BLENDS AND ITS APPLICATION FOR POLY (VINYL CHLORIDE) (PVC) PLASTICIZATION

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ABSTRACT

In this thesis, the properties of binary blends of epoxidized natural rubber (ENR) and genistein have been explored by thermal gravimetric analysis (TGA), polarized optical microscope (POM), differential scanning calorimetry (DSC), advanced polymer analyzer (APA) and dynamic mechanical analysis (DMA). Although the melt blends of ENR/genistein are partially miscible, the functional groups of the constituents can react with each other at elevated temperatures above 220 °C, resulting in cured ENR networks by genistein. The cured network showed systematic movement of the glass transition temperatures and also melting point depression at genistein rich compositions, suggestive of miscible character. The theoretical binary phase diagram was constructed in comparison with the observed melting points depression in the framework of Flory-Huggins theory of mixing and the phase field theory of crystallization. The crystal-amorphous interaction parameter was determined based on the melting point depression and heat of fusions as a function of blend compositions. The ENR/genistein system was applied to the plasticization of poly (vinyl chloride) (PVC). Due to the thermal instability of pure PVC, additional stabilizer should be used to mix PVC in an internal mixer (Brabender Plasticorder). Epoxidized soybean oil (ESBO) was chosen a stabilizer/plasticizer to PVC. The systematic shift of glass transition temperatures of PVC/ESBO/ENR/genistein was noticed in both DSC and DMA runs. ENR/genistein blends were found to suppress the glass transition temperature of PVC effectively. Last not least, the mechanical properties of PVC/ESBO/ENR/genistein blends were measured by using Instron tensile tester and the observed change of brittle to ductile properties with compositions was discussed.
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CHAPTER I

INTRODUCTION

It is quite common to mix two or more polymers to achieve a preferred property in these days. A way to characterize polymer blends is measuring miscibility. Flory-Huggins Theory is a starting point to discuss whether the mixture is miscible or not. But only a few miscible systems can be explicable by the simplest Flory’s model. For most systems, modifications have to be made to improve Flory-Huggins theory in order to make it valid for a specific system.

Poly (vinyl chloride), PVC is one of the most widely used plastic materials in the world. It can hardly be handled in pure form since it has very rigid structure and poor thermal stability. Plasticizers are required to make it softer and more flexible. The most traditional plasticizers are phthalate derivatives which are hazardous and can easily leach away. As PVC has been applied in multiple fields in our daily life, there is an urgent need to develop an environmentally friendly plasticizer to replace phthalates. Epoxidized natural rubber (ENR) is one of the choices. Literature has indicated that PVC and ENR are miscible since ENR can lower the glass transition temperature of PVC which means ENR may be an efficient plasticizer of PVC.

In literature, ENR/PVC blends are processed by solution casting or melt-mixing methods. As solution casting method is difficult to be put into practice in manufacturing, melting-mixing method is preferred. However, stabilizers are required to process PVC in melt owing to its poor thermal stability. Genistein is taken into
consideration. Genistein is a kind of crystalline molecule extracted from plants such as soy bean or sugar beets with yellowish color and aromatic odor.[1] It is known for its excellent antioxidant activity as it can track and scavenge free radicals.[2] The properties of ENR/Genistein blends are explored in this thesis. Nevertheless, genistein alone is not enough to make stable plasticized system of plasticized PVC. Epoxidized soy bean oil (ESBO) having small amount of epoxidized groups should be added in this system. Both genistein and ESBO are environmentally friendly. In this way, we establish a stable and green system for plasticized PVC, which is a central theme of this research.

In this thesis, Chapter I introduces the idea of the research. Chapter II goes through the literatures pertaining to ENR/genistein system, polymer blends and plasticizers for PVC. Chapter III describes the samples preparation and characterization. As to Chapter IV, the thermal property of ENR/genistein blend is discussed. In Chapter V, a modified Flory-Huggins theory by Matkar and Kyu is employed to draw the phase diagram of ENR/genistein blends. Chapter VI elucidates the way of constructing a plasticized PVC system. The summary and future recommendations are included in Chapter VII.
CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Introduction to ENR and Genistein

This part will introduce ENR and Genistein respectively as the two mainly used materials. The two materials are supposed to react with each other due to the functional groups in their structures.

2.1.1 Introduction to ENR

Epoxidized natural rubber (ENR) is a modified natural rubber (NR) with epoxide groups dispersed randomly in the molecule chain.[3] (Figure 2.1) The chemical modification of natural rubber was investigated long time ago due to the demand for polymer materials to face the oil crisis. Epoxidation is one desirable approach owing to its easy reaction condition and relatively low cost. A typical chemical principle of ENR from NR is to use peracetic acid which is displayed in Figure 2.2(a). However, the subsequent ring-opening reactions may occur during the reaction which would affect the purity of ENR. (Figure 2.2(b)) But recent study has given a way to avoid the ring-opening reactions so that we can obtain clean ENR at any grade of epoxidation.

Normally there are two levels of commercial ENR products having different epoxide contents: 25% mole (ENR 25) and 50% mole (ENR 50).[3]
Figure 2.1 Chemical structure of ENR showing epoxide groups dispersed in the molecular chain.

Figure 2.1 (a) Schematic Formation of ENR from NR, and (b) Ring-openings reaction of ENR introducing by-products[4]

As epoxide groups substitute the unsaturated double bonds, the properties of ENR are quite different from natural rubber. The epoxide group has stronger polarity which means the molecular chain is less flexible leading to the increase of glass transition temperature ($T_g$) and solubility parameter.[4] For instance, the glass transition temperature of NR is -70°C whereas ENR 25 has the $T_g$ of -47°C. For ENR50, $T_g$ is -24°C. The glass transition temperature and solubility parameter distinction influences the physical properties. As solubility parameter increases with epoxidation, ENR with higher epoxidation level shows poorer compatibility with nonpolar polymers which exhibits excellent oil resistance. Epoxide groups can also prevent crystallization of NR. ENR 50
can be reserved at $0^\circ$C for 3 months without crystallization. Another difference between ENR and NR is the phenomenon of storage hardening. The Mooney viscosity of NR increases if it is stored for a long time.[5] The mechanism is that the abnormal groups such as aldehyde groups in NR will react with proteins forming crosslinks in the rubber. ENR does not show this phenomenon and Subramaniam[6] indicated that epoxide group is not the factor. In processing, ENR has similar properties as NR except that ENR with low viscosity might be sticky. Thus a processing aid is required during processing. With the addition of epoxide groups, the number of unsaturated double bonds reduces, which improves the anti-oxidation. ENR can be cured by any of the standard curing agent. ENR with high sulphur vulcanized system is not recommended because of the poor ageing resistance. The strength properties and strain crystallization after curing reduce with epoxidation in NR. This is because the stereo-regularity in NR structure is disturbed by epoxide groups. However, the reduction of strain-induced crystallization can be recognized only when the epoxidation level is over 50% which implies four isoprene units can endure two epoxide groups without excess interruption. The properties of vulcanizates of ENR are determined by the strain-induced crystallization after curing and glass transition temperature and solubility parameter in epoxidation reaction.

ENR can be applied in many varied areas due to its specific structure. The epoxide groups can act as crosslinking sites which will be discussed in the following chapter. Its resistance of oxidation makes rubber bound antioxidants. Epoxide groups also give a chance for further modification.
2.1.2 Introduction to Genistein

Recently we have paid considerable attention on phytochemicals which are derived from plants. Phytochemicals own the merits of low toxicity, abundant source and ease of extraction which provoked our interest to maximize applications of these presents from nature.[7] One phytochemical that belongs to the isoflavone class is genistein. Genistein, with IUPAC name of 5, 7-Dihydroxy-3-(4-hydroxyphenyl) chromen-4-one (Figure 2.3), is a natural product from soy. Its needle-like crystal has a typical orthorhombic unit cell with hierarchical spherulitic morphology with Maltese cross and birefringent colors as shown in Figure 2.4.

![Figure 2.2 Chemical structure of Genistein displaying phenolic hydroxyl groups](image)

The extraction means of genistein are mainly acid treatment, enzyme treatment, and chemical synthesis. But acid treatment is hard to obtain pure product and the cost of other two is relatively high.[8] A novel way to extract genistein by fermentation has been investigated by Pandit and Patravale and the product has high purity as 91.04% and the
extraction efficiency can reach 67.01%. Genistein, as a kind of phytoestrogen, has been reported to possess various biological activities such as inhibition of tyrosine kinases, activation of estrogen beta, simulation of autophagy[10–12], etc. Therefore, genistein is extensively evaluated for chemoprevention of breast, uterine and prostate cancers.[13] However, when it comes to carcinogenic and toxic potential, it has been found to be poisonous to normal cells in high doses.[14] It is a suspect for infant leukemia during pregnancy.[15][16] Genistein has great antioxidant capacities by reason of its phenolic hydroxyl groups in the structure.[17] The hydroxyl group can scavenge the free radicals which would start chain reaction by donating a hydrogen atom to free radicals.[18] (Figure 2.5) The antioxidant capacity can be measured by several means including spectrophotometric assays such as cyclic voltammetry.[19] As to cyclic voltammetry, the redox potentials are considered to characterize the free radical scavenging capacity. The lower peak potential indicates the higher antioxidant activity.

\[
\text{ROH} \rightarrow \text{RO}^* + \text{H}^* 
\]

Figure 2.4 Hydrogen atom donation mechanism[17] of hydroxyl group

2.1.3 The possible reaction mechanism between ENR and Genistein

Literature has proved that phenolic hydroxyl groups can undergo the oxirane ring opening reaction with the epoxide groups. The reaction scheme is shown as follows:[20]
Figure 2.5 Possible reaction between epoxide group and phenol hydroxyl group indicating ring-opening reaction

The advantage of this phenol-epoxy reaction is that the two reactive groups are stable and the reaction technique is easy. As ENR has epoxide groups in the structure and genistein has phenols, it is reasonable to suppose that ENR can react with genistein which means genistein may act as a curing agent for ENR. In this thesis, the reaction between ENR and genistein is explored.

2.2 Thermodynamics of Polymer Blends

2.2.1 Introduction to Flory-Huggins Theory

Polymer blends are defined as combination of two or more polymers and miscibility is the considerable subject for polymer mixtures.[21] A completely immiscible system has several amorphous phases and each phase contains one pure component. One phase of a partially miscible system may contain some amount of each constituent. The completely miscible blends exhibit only one amorphous phase.

Flory-Huggins Theory is a mathematical model to describe miscibility in polymer blends.

When different components mix together, the formation of molecular scale blends depends on the Gibbs free energy change of mixing, $\Delta G_m$, which is defined as

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2.1)$$
where $\Delta H_m$ is the energy of mixing, $\Delta S_m$ is the entropy of mixing and $T$ is the absolute temperature.

For a spontaneous mixing, $\Delta G_m$ should be negative. However, it is not necessary to form a homogeneous phase just with a negative $\Delta G_m$. Another requirement should also be met. Only when

$$(\frac{\partial^2 \Delta G_m}{\partial \phi^2})_{T,P} > 0$$

(2.2)

where $\phi$ is the volume fraction of either component, a stable one phase mixture persists.

In Flory-Huggins theory[22][23], $\Delta S_m$ is expressed as

$$\Delta S_m = -k(\phi_1 \ln \phi_1/r_1 + \phi_2 \ln \phi_2/r_2)$$

(2.3)

where $\phi_1$ and $\phi_2$ represent the volume fractions of each component. $r_1$ and $r_2$ show the numbers of statistical segments of each single polymer chain. $k$ is the Boltzmann constant.

$$\Delta H_m = \phi_1 \phi_2 \chi kT$$

(2.4)

where $\chi$ is the interaction parameter.

By combining equation (2.3) and (2.4), we can get

$$\frac{\Delta G_m}{kT} = (\phi_1 \ln \phi_1/r_1 + \phi_2 \ln \phi_2/r_2) + \phi_1 \phi_2 \chi$$

(2.5)

For a binary system,

$$\phi_1 + \phi_2 = 1$$

(2.6)

The Flory-Huggins free energy of mixing can be demonstrated as

$$f_{\text{mixing}} = \phi \ln \phi/r_1 + (1- \phi) \ln(1- \phi)/r_2 + \phi(1-\phi)\chi_{FH}$$

(2.7)

$\chi_{FH}$ plays a very significant role in determination of free energy of mixing. According to Flory-Huggins theory, we assume that there is no volume change in mixing. When we look at $\chi_{FH}$ in view of interaction energy, $\chi_{FH}$ is described as
\[ \chi_{FH} = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \]  

(2.8)

where \( \delta_1 \) and \( \delta_2 \) are the solubility parameter of each component, \( V_1 \) is the lattice size defined by the solvent size and \( R \) is the universal gas constant. However, the estimation of \( \chi_{FH} \) from equation (2.8) is not quantitatively reliable compared with experiment values. An empirical equation is found to calculate \( \chi_{FH} \) when the predicted value is less than 0.3:

\[ \chi_{FH} = 0.34 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \]  

(2.9)

Nevertheless, both equation (2.8) and (2.9) cannot explain the LCST (lower critical solution temperature) behavior which leads \( \chi_{FH} \)-T relation to a modified equation:

\[ \chi_{FH} = A + \frac{B}{T} \]  

(2.10)

Both \( A \) and \( B \) are constants which may be positive or negative. \( A \) is the entropic correction factor and

\[ B = (\chi_c - A) T_{crit} \]  

(2.11)

where \( \chi_c \) is the critical value of \( \chi_{FH} \) at \( T_{crit} \):

\[ \chi_c = 0.5 \left( \frac{1}{\sqrt{\tau_1}} + \frac{1}{\sqrt{\tau_2}} \right)^2 \]  

(2.12)

From equation (2.7), \( \chi_{FH} \) determines the sign of \( \Delta G_m \): if \( \chi_{FH} \) is negative, \( \Delta G_m \) should be negative which means the mixing is spontaneous at any temperature and compositions. If \( \chi_{FH} \) is positive, \( \Delta G_m \) is not necessarily negative and the mixing is probably nonspontaneous in some conditions.

To discuss how to form a homogeneous system, we can draw the \( \Delta G_m - \phi \) curve. (Figure 2.7) At \( T_1 \), the mixture is homogeneous at any composition due to the single minimum in the curve. There are 2 minimums lying at \( \phi' \) and \( \phi'' \) respectively at \( T_2 \), which indicates that two phases may coexist at equilibrium when the composition is between \( \phi' \)}
and $\phi''$. For phase equilibria, the chemical potential of component 1 is the same in both phases and so is component 2. That is

$$\mu_1(\phi') = \mu_1(\phi'') \quad (2.13)$$

$$\mu_2(\phi') = \mu_2(\phi'') \quad (2.14)$$

Equation (2.13) and (2.14) imply the first order partial derivative of $\Delta G_m$. Figure 2.8 demonstrates the phase diagram of UCST (upper critical solution temperature). By solving Equation (2.13) and (2.14), the binodal curve which separates the one-phase region from the two-phase region can be obtained. To find the spinodal, the second order partial derivative of $\Delta G_m$ should be zero. That is to say,

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi^2}\right)_{T,P} = 0 \quad (2.15)$$

The spinodal is the line between the unstable area and metastable area. For any infinitesimal concentration fluctuation in unstable area, the mixture will spontaneously phase separate which is called spinodal decomposition (SD) while a finite fluctuation leading to phase separation in metastable region is called nucleation growth (NG). The binodal and spinodal meet at the critical point:

$$\left(\frac{\partial^3 \Delta G_m}{\partial \phi^3}\right)_{T,P} = 0 \quad (2.16)$$

By solving (2.13), (2.14) and letting (2.15) and (2.16) equal zero, $\phi_c$ can be calculated as follows:

$$\phi_c = \frac{\sqrt{\gamma_2}}{\sqrt{\gamma_1} + \sqrt{\gamma_2}} \quad (2.17)$$

Figure 2.9 shows several kinds of phase diagrams according to $\chi$ variation with temperature. $\chi$ is temperature dependent and affects the shape of phase diagram. Figure 2.9(a) displays UCST behavior indicating the blend is miscible above critical temperature and not miscible at lower temperatures. Figure 2.9(b) is LCST which is as
opposed to UCST. Figure 2.9(c), (d) and (e) elucidate the combination of both UCST and LCST. Figure 2.9(d) is the closed miscibility loop. Figure 2.9(e) is the hour-glass diagram.

Figure 2.6 Schematic relation between free energy of mixing and composition

Figure 2.7 Phase diagram of a classical upper critical solution temperature (UCST)
Figure 2.8 Effects of temperature dependence of $\chi$ on the phase diagrams (a) is UCST behavior indicating the blend is miscible above critical temperature and not miscible at lower temperatures; (b) is LCST which is as opposed to UCST; (c), (d) and (e) elucidate the combination of both UCST and LCST whereas (d) is the closed miscibility loop and (e) is the hour-glass diagram.
2.2.2 Modification of Flory-Huggins theory for crystal-amorphous blends

Although Flory-Huggins theory is widely used in miscibility of amorphous-amorphous polymer blends, there is some problem to account for the phase equilibria of crystal-amorphous blends. The Flory diluent theory keeps the assumption of total insolubility of solvent in crystal.\[24\] Based on this assumption, $\chi_{\text{FH}}$ can be calculated directly from melting points data of crystal in polymer blends. Nishi and Wang\[25\] applied this theory to actual polymer blends of poly(vinylidene fluoride)(PVDF) and poly(methyl methacrylate)(PMMA). However, $\chi_{\text{FH}}$ values obtained from this way are larger than those from experiment such as X-ray and small-angle neutron scattering in order of magnitude. Another deficiency of this theory is that although liquidus line may be drawn from calculation, it failed to predict solidus line as Flory assumed that there is little solvent in the crystal so that the solidus line coincides with the axis of neat crystal component. Guenet et al. studied the possibility of solvent remaining in crystal and constructed phase diagram of syndiotactic polystyrene (sPS) and naphthalene blends. Both liquidus and solidus lines can be seen from experiment data.

Encouraged by the result, Matkar and Kyu\[26\] removed the assumption of total rejection of solvent in crystal and considered not only amorphous-amorphous interaction but also crystal solidification and crystal-amorphous interaction. To determine free energy of crystal solidification, the crystal phase order parameter $\psi$ can be defined as the ratio of the lamellar thickness of polymer crystal ($l$) to the lamellar thickness of the perfect crystal ($l_0$) which is in accordance with the linear crystallinity and $0 \leq \psi \leq 1$. $\psi=0$ represents the melt state whereas $\psi=1$ represents the complete crystal state. To derive the free energy density for crystal solidification, Landau type phase field free energy was
applied. Figure 2.10 is a Landau-type asymmetric double-well curve which indicates a two-phase structure in the blends. The free energy equation is

\[ f_{\text{crystal}} = W\left\{ \frac{\psi^4}{4} - (\xi + \xi_0) \frac{\psi^3}{3} + \xi \xi_0 \frac{\psi^2}{2} \right\} \]  

(2.18)

where \( W \) is the barrier for crystallization, and \( \xi, \xi_0 \) indicate the minimum and maximum potential well on the \( \psi \) axis respectively. Figure 2.11 demonstrates the diagram of \( f_{\text{crystal}} - \psi \). At melting temperature, the well is symmetric and the potentials of \( \psi = 0 \) and \( \psi = 1 \) are both equal to 0 which means the melt state and crystal state coexist and reach to equilibrium. At \( T < T_m^0 \) (the equilibrium melting temperature), the free energy of \( \psi = \xi_0 \) is lower than melt state and it prefers to form crystal. Define that \( \phi \) is the volume fraction of crystalline component and \((1 - \phi)\) is that of amorphous one. The free energy for polymer crystallization can be expressed as \( \phi f_{\text{crystal}} \).

Figure 2.9 A Landau-type double-well free energy of mixing
As to crystal-amorphous interaction, an equation is given to determine the free energy:

\[ f_{\text{interaction}} = \chi_{ca} \phi (1-\phi) \psi^2 \]  \hspace{1cm} (2.19)

where \( \chi_{ca} \) is the interaction parameter for crystal-amorphous interaction. \( \phi \psi \) can be interpreted as crystallinity while \( (1-\phi) \psi \) can be regarded as the interaction of crystal with amorphous part.

By combining the three terms together, an expression of total free energy can be written as follows:

\[ f_{\text{overall}}(\phi, \psi) = f_{\text{mixing}} + \phi f_{\text{crystal}} + f_{\text{interaction}} \]  \hspace{1cm} (2.20)

that is

\[ f_{\text{overall}}(\phi, \psi) = [\phi \ln \phi / r_1 + (1-\phi) \ln (1-\phi) / r_2 + \phi (1-\phi) \chi_{\text{FH}}] + \phi W [\frac{\psi^4}{4} - (\zeta + \zeta_0) \frac{\psi^3}{3} + \zeta \zeta_0 \frac{\psi^2}{2}] + \chi_{ca} \phi (1-\phi) \psi^2 \]  \hspace{1cm} (2.21)
To achieve the solid-liquid phase transition line, the minimum of free energy pertaining to solidification and crystal-liquid interaction should be calculated. Interpreted by equation is that,

\[ \frac{\partial f(\psi)}{\partial \psi} = 0 = W \left[ \frac{\xi_0^2}{4} - \left( \xi + \xi_0 \right) \psi + \psi^2 \right] + 2 \chi_{ca} (1 - \phi) \tag{2.22} \]

At the equilibrium state, when \( \psi=0 \) (melt state) and \( \xi_0 \) (crystal state), \( \frac{\partial f}{\partial \psi} = 0 \) and \( f = 0 \) can be satisfied at the same time. From equation (2.21),

\[ W \left[ \frac{\xi_0^2}{4} - \left( \xi + \xi_0 \right) \frac{\xi_0}{3} + \frac{\xi_0 \xi_0}{2} \right] + \chi_{ca} (1-\phi) = 0 \tag{2.23} \]

And

\[ W = \frac{6\Delta H_u}{RT} \left(1 - \frac{T}{T_m} \right) \left( \frac{1}{2} - \xi \right)^{-1} \tag{2.24} \]

where \( \Delta H_u \) is the heat of fusion.

Combination of equation (2.23) and (2.24) and letting \( T=T_m \) leads to

\[ (1 - \frac{T_m}{T_m}) = \frac{RT_m}{6\Delta H_u} \left( \xi - \frac{1}{2} \right) \left[ \frac{\xi_0^2}{4} - \left( \xi + \xi_0 \right) \frac{\xi_0}{3} + \frac{\xi_0 \xi_0}{2} \right]^{-1} \chi_{ca} \left(1-\phi\right) \tag{2.25} \]

Simplify this equation by letting \( \xi_0 = 1 \),

\[ (1 - \frac{T_m}{T_m}) = \frac{RT_m}{\Delta H_u} \chi_{ca} (1-\phi) \tag{2.26} \]

However, equation (2.26) is limited to high polymer crystals as \( \xi_0 < 1 \) in polymer crystals.

From equation (2.26), \( \chi_{ca} \) is possible to be obtained from a set of experiment data. When getting melting points of several compositions, the plot of \( (1 - \frac{T_m}{T_m}) \) vs \( (1-\phi) \) can be drawn. The slope can be noted as \( B_c \), then

\[ \chi_{ca} = B_c \frac{\Delta H_u}{RT_m} \tag{2.27} \]

When it comes to the construction of phase diagrams, the total free energy should be minimized. At first, the free energy pertaining to \( \psi \) should be minimized by calculating
\[ \frac{\partial (\phi \psi)}{\partial \psi} = 0. \]  When obtaining the minimal free energy for each \( \phi \), the chemical potentials can be determined so that the phase diagrams can be established.

There are different phase diagrams for crystal-amorphous blends due to the interaction between crystal-amorphous and amorphous-amorphous phase transitions. Figure 2.12 demonstrates the effect of UCST on crystal-amorphous phase transition in crystal-amorphous blends. In Figure 2.12(a), the two components are completely compatible showing no liquid-liquid phase separation curve. The UCST line is far below the melting temperatures. Therefore, the liquidus line and solidus line overlap with each other. There is only melting points depression of crystalline constituent in the phase diagram with no coexistence region. In Figure 2.12(b), UCST shows up and starts to affect the solid-liquid phase transition although they do not meet in the phase diagram. There is a gap between liquidus line and solidus line which is considered as coexistence of amorphous component and crystal. In Figure 2.12(c), liquid-solid transition area meets with UCST and interplay with each other. The dotted line implies the UCST region from which we can figure out the interaction between solid-liquid phase transition and UCST is not simply overlapped to exhibit the coexistence region. When it comes to Figure 2.12(d), UCST shows the protrusion above liquid-solid region indicating the coexistence of two constituents in liquid state.
Figure 2.11 Interaction between UCST and liquid-solid phase transition (a) showing a superimposition of the liquidus and solidus lines; (b) broadening of the crystal + liquid coexistence zone by the liquidus and solidus lines with pronounced effect of UCST, (c) showing an interaction between the solid-liquid phase transition, and (d) protrusion of the UCST above the solidus and liquidus lines showing various coexistence regions such as liquid + liquid, liquid + solid, and pure solid zones[27]

2.3 Overview of plasticization of PVC

Plasticizer is a kind of additive applied to plastics especially PVC to decrease the glass transition temperature in order to obtain high fluidity.[28] In this part, the plasticization of PVC would be introduced.
2.3.1 The mechanism of plasticizer action and processing method

Usually a plasticizer is a small molecule added to polymer materials to interact with the polymer chains on the molecular level to increase its chain mobility. A polymeric plasticizer is a high molecular weight material with the advantage of permanence because of its low vapor pressure and diffusion rate compared with small molecule plasticizers. The classical theories of mechanisms of plasticizers action are the lubricity theory and the gel theory. The lubricity theory[29] considers that the intermolecular friction would decrease due to plasticizers. According to the gel theory[30–32], the rigidity of polymer is determined by tridimensional structures along the chains. The plasticizer can reduce the attachments between the polymer molecules so that the polymer can be deformed more easily. However, a more precise theory to explain plasticization mechanism is the free volume theory. It is believed that below T_g, the specific volume of polymers increases linearly at a lower rate. But when the temperature reaches T_g, the slope of specific volume-temperature curve has a sharp rise. (Figure 2.13) When the specific volume-temperature curves are extrapolated, the intercept at absolute zero temperature is the same for all polymers which is regarded as the space between atoms and molecules without movement. Also the volume at the transition temperature is constant and the volume difference between absolute zero temperature and the glass transition temperature is considered as the space for oscillations. From discussion above, the free volume can be defined as the space between atoms and molecules. It can be divided into two parts[33]: before transition temperature it increases slightly with the temperature due to oscillations; and after transition temperature it increases greatly with the formation of holes. The effect of polymer structure on glass transition temperature can be explained by the free
volume theory[34]. Free volume is provided by three motions in polymer chains: (1) the motion of chain ends; (2) the motion of side chains; (3) the motion of the main chain. For instance, crosslinked polymers have fewer endgroups resulting in less pronounced free volume influence which show high glass transition temperatures. The study of plasticization aims to increase the free volume in polymer chains by improving the aforementioned three motions. For increasing the number of end groups, one can lower the molecular weight. By internal plasticization the number of side chains and the main chain mobility can be increased. The addition of a compatible small molecule can also achieve the same results. Therefore, the plasticizer in the polymer not only introduces molecules with lower $T_g$, but increases the free volume in the system greatly. In the case of PVC, the polar groups in the structure play a significant role for good compatibility. Chlorine atoms can reduce van der Waals forces by separating the chains and the dipoles can be considered as points of attraction. With the addition of plasticizer, the plasticizer molecules can line up dipoles with dipoles from PVC. (Figure 2.14)[35] Then polymer chains are more mobile than they are in base polymer form. The polar and polarizable groups of plasticizer can increase tensile strength while the non-polar groups determine the flexibility. The processing method for plasticization used in this thesis is compounding. Compounding/mixing process is actually a complex process although it seems simple. Various factors should be taken into consideration including equipment choosing, mixing design and sequence of adding materials.[36] [37]
Figure 2.12 General specific volume-temperature curve showing a sharp rise at the slope of specific volume-temperature curve when the temperature reaches $T_g$

Figure 2.13 Schematic representation of polymer and plasticizer points of interaction[35]

2.3.2 Recent development of plasticizers for PVC

Poly(vinyl chloride), PVC(Figure 2.15) is the third-most widely used plastic materials in the world[38]. It cannot be processed in pure form due to the rigid structure and poor thermal stability. Therefore, plasticizers are required to increase the plasticity or fluidity of PVC. The most commonly used are phthalates.[39] Figure 2.16 displays the general chemical structure of phthalates. But phthalates are hazardous as report said that phthalates can cause endocrine disruption, which might result in breast cancer. Also high
amounts of phthalates can damage liver and testes. What is worse, phthalates are easily released to the environment because of the vulnerably physical force between plasticizers and plastics. As PVC has been applied in multiple fields such as medical devices, electronics, food packaging, toys, cosmetic products and etc., most people are found to have diverse phthalates in their urine. Now a huge concern has been raised about leaching of phthalates. Thus, there is an urgent need to develop an environmentally friendly plasticizer to replace phthalates. Several alternative plasticizers have been developed to substitute phthalates such as benzoates, adipates and trimellitate. But they have difficulties reaching the market due to high price or unsatisfactory compatibility issues.

\[
\begin{array}{c}
\text{CH}_2 \\
n \text{CH} \\
\text{Cl}
\end{array}
\]

Figure 2.14 Chemical structure of PVC

\[
\begin{array}{c}
\text{O} \\
\text{OR} \\
\text{OR'} \\
\text{O}
\end{array}
\]

Figure 2.15 General chemical structure of phthalates (R and R’ are general placeholders)

Rubber plasticizer for PVC has also been considered before. Acrylonitrile-butadiene rubber, NBR and styrene-acrylonitrile rubber, SAN are proved to modify PVC in its processing and elastic properties.[40] Butadiene/acrylonitrile copolymers have been used for permanent plasticization of PVC. The NBR/PVC mixtures manifest a lot of
interesting properties including improved resistance to sunlight and ozone, tear, flex cracking and aging.[41] The applications consist of wire and cable insulation, food vessels, pipes for oil, etc.[42]

Epoxides have been considered as good alternatives as they are non-toxic. Epoxidized soybean oil is one of the suitable choices.[43] From these findings, ENR might be supposed to plasticizing PVC as a replacement for phthalates.

2.3.3 Properties of ENR/PVC blends

Literature has indicated that PVC and ENR are miscible with each other. This is because the acidic hydrogens of PVC can form hydrogen bonding with oxirane groups of ENR. Margaritis and Kalfoglou made ENR 50/PVC blends and ENR 25/PVC blends for all composition range by solution casting method and found that ENR 50 is miscible at all ratio while ENR 25 is miscible only at low rubber amounts.[44] Varughese and Nando reported that the $T_g$ decreased with increasing ENR 50 concentration in the ENR 50/PVC melt blends.(Figure 2.17)[45]
Figure 2.16 Variation of Tg in ENR/PVC blends, showing a closer fit with Gordon-Taylor equation.

As can be seen in Figure 2.17, the TgS of the ENR/PVC blends are in line with Gordon-Taylor equation which is presented in equation (2.28) relative to Fox relationship (equation(2.29)).[46] [47]

\[ T_{gb} = \frac{T_{g1} + kT_{g2}W_2}{W_1 + kW_2} \]  \hspace{2cm} (2.28)

\[ \frac{1}{T_{gb}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \]  \hspace{2cm} (2.29)

Where \( T_{gb}, T_{g1}\) and \( T_{g2}\) are the glass transition temperatures of blend and each component respectively, \( W_1 \) and \( W_2 \) are weight fractions of each component and \( k \) is the adjustable parameter.

From Dynamic Mechanical Analysis results made by Senake et al, there is some degree of heterogeneity in the ENR/PVC blends as manifested by broadening of the glass transition zone.[48] The level of broadening is increased with increasing PVC amount.[45]
This may result from crystallites of PVC.[45] Varughese et al also discussed several properties of plasticized ENR/PVC blends. The experimental data of density was higher than that of calculated one due to condensation of molecules in ENR/PVC blends. The $T_g$ shifted to a lower temperature relative to rigid ENR/PVC blends, showing greater flexibility. The width of $T_g$ decreased with ENR content. This is because plasticizer trapped in ENR rich region increased the compatibility between ENR and PVC.[49] The melt rheology including viscosity and elasticity was tested. The viscosity increased with temperature while the elasticity varied in a complicated manner. The elasticity of ENR up to 50% content increased with temperature. However, in higher ENR contents, the die swell ratio and recoverable shear strain reduced with temperature while the principle normal stress difference and elastic shear modulus remained unchange.[50] The study of tensile and tear failure of plasticized ENR/PVC gave the idea that the fracture surfaces would not interfere in the miscibility of ENR/PVC blends.[51] As there are numerous unsaturated bonds in ENR, ENR/PVC blends can be vulcanized by using a curing agent such as dimaleimide. There was no discernible phase separation after curing. But the microheterogeneity reduced as interfacial adhesion increased. The elastic deformation as well as thermal stability improved in terms of crosslinking.[52] Most of these plasticized blends used dioctyl phthalate (DOP) as plasticizer. Ishiaku et al compared epoxidized soya oil (ESO) with DOP with respect to ageing time of the blends. ESO exhibited poorer ageing behavior but better compatibility with ENR/PVC blends.[53] Although the compatibility of ENR and PVC has been explored, no one has attempted to use ENR as plasticizer for PVC due to the difficulty for processing.
2.3.4 Stabilizers for plasticized PVC system

One of the problems encountered in processing of PVC is that PVC starts to decompose at 70 °C which is much lower than the required processing temperature. This is because the defect sites in PVC can easily eliminate chlorine and hydrogen and release noxious hydrogen chloride. Once dehydrochlorination begins, it is autocatalytic. Consequently, the use of stabilizers is essential to prevent the decomposition reaction during the fabrication. A lot of types of stabilizers have been put into practice over the past eighty years. The main stabilizer types are leads, barium-cadmium mixed metals, calcium-zinc mixed metals, organotins, etc.[54] There are no universally applicable stabilizer as the choice of stabilizer depends on the technical requirements of product regulatory approval requirements and cost. When it came to the stabilization of ENR/PVC blends, Ratnam and Zaman presented stability of ENR/PVC bends added by several kinds of stabilizers. They concluded that tribasic lead sulfate was the best stabilizer, but it was toxic.[55]

In this thesis, genistein and ESBO are regarded as stabilizers in processing. Both of them are non-toxic and have stabilizing effect on PVC. ESBO is a kind of vegetable oil extracted from soybean (Figure 2.18). It is considered as a secondary plasticizer and stabilizer as its epoxide groups can react with hydrogen chloride which eliminates the chain reaction of degradation of PVC. However, ESBO alone is not enough for stabilization and inclusion of Ba/Cd and Ca/Zn stearates or other organic stabilizers is required.
Figure 2.17 Chemical structure of ESBO
CHAPTER III

MATERIALS AND EXPERIMENTAL TECHNIQUES

3.1 Materials

Genistein was obtained from Riotto Botanical CO., LTD. with 98% purity; epoxidized natural rubber, ENR, with 50 mole% epoxidation was provided by Sanyo Corporation; poly (vinyl chloride), PVC with K-value 56 was kindly supplied by Formosa Plastics; epoxidized soybean oil, ESBO was purchased from The Chemical Company.

3.2 Blends preparation

ENR/genistein blends were prepared at 120°C for 9 min in a Brabender Plasticorder Model PL 2000. The rotor speed was 45 r.p.m. APA, DMA samples of ENR/genistein blends were made by compression molding at 150 °C under 20,000 pounds pressure for 30 min. POM samples were made by solution casting. ENR (1 g) was dissolved in 100 ml of toluene and genistein (6 g) was dissolved in 100 ml tetrahydrofuran. The two solutions were mixed together at various compositions. Then the solution was cast onto a glass slide and placed in a fume hood overnight to remove solvent. To dry the blends completely, the solution was then moved in vacuum oven over night at 100°C. The samples would be cured in an oven at 250 °C for 10 min.
ENR/PVC blends were prepared by solution casting. ENR (1 g) was dissolved in 100 ml of toluene and PVC (10 g) was dissolved in 100 ml tetrahydrofuran. The two solutions were mixed together at various compositions: ENR/PVC 0/100, 30/70, 50/50, 70/30, 100/0. Then the solution was cast onto a glass slide and placed in a fume hood overnight to remove solvent. To dry the blends completely, the solution was then moved in vacuum oven over night at 100°C.

ENR/PVC/genistein/ESBO blends were prepared at 150 °C for 5 min n a Brabender Plasticorder Model PL 2000. The rotor speed was 45 r.p.m. DMA, Instron samples were made by compression molding at 150 °C under 50,000 pounds pressure for 5 min.

3.3 Blends characterization

The blends were characterized by TGA, DSC, POM, APA, DMA, Instron instruments. The introduction and experiment settings of each instrument are listed as follows.

3.3.1 Thermogravimetric Analyzer (TGA) measurements

The TGA measurements were performed in a Q50 v20.10 Build 36 model (TA instruments). The sample was heated in platinum pan with 60.0 ml/min nitrogen at 10 °C/min to 600 °C. The sample amount was weighed approximately 10 mg.
3.3.2 Differential Scanning Calorimetry (DSC) measurements

The DSC apparatus was a Q200 v24.4 Build 116 model (TA instruments) purged with nitrogen gas at a rate of 40.0 ml/min and calibrated with indium standard. Aluminum Hermetic pans were used to seal the samples, an empty one serving as a reference. For ENR/genistein blends, the heating cycle applied was 40 °C→100 °C→50 °C(2 min)→320 °C. For ENR/PVC blends, the heating cycle applied was 40 °C→90 °C(2 min) →-50 °C→200 °C. For ENR/genistein/PVC/ESBO blends, the heating cycle applied was 40 °C→100 °C(2 min)→-50 °C(2 min)→200 °C. The scan rate was 10 °C/min if without specific annotation. T_g was determined from the second heating scan as the first scan was conducted to remove thermal history.

3.3.3 Polarized Optical Microscope (POM)

POM (BX60, Olympus) was employed to observe the phase morphology of crystal. The photographs of microstructures were taken by a digital camera (EOS 400D, Canon) under suitable magnifications (i.e., 500x) after crossed polarization.

3.3.4 Advanced Polymer Analyzer (APA) tests

The APA tests were carried out environment at 250 °C, a frequency of 1.67 Hz and 6.98% angle on the APA 2000. The instrument measured the curing time of each sample by monitoring the storage torque amplitude (S’) of the mixtures.

3.3.5 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) was conducted with a Q800 V20.26 Build 45 model (TA instruments) dynamic mechanical analyzer at an oscillation strain of
0.5%. The temperature range studied was from -30 °C to 150 °C with a heating rate of 3 °C /min.

3.3.6 Instron

Tensile properties were determined with an Instron tester (model 5567) with a load of 1000N at a crosshead rate of 10 mm/min. All Instron tests were conducted at ambient temperature (20–25 °C) and the average value of three repeated tests was taken for each composition.
CHAPTER IV

THERMAL PROPERTIES OF ENR/GENISTEIN BLENDS

4.1 Introduction

Mixing is an easy way to produce new materials with different physical properties. Usually the melt blending is just physically bonded. For a polymer blend, the miscibility can be reflected in the glass transition temperature. A miscible binary system would illustrate single glass transition temperature which is between $T_g$ of each constituent. In our system, genistein is a small molecule without a $T_g$. It can be considered that $T_g$ of genistein is infinitesimal it can lower the $T_g$ of ENR. This is a typical characteristic for small molecule plasticizer.

In this chapter, first of all, the thermal stability was measured. From TGA results, we can see whether there is an improvement in stability after the mixing process. And then the miscibility of ENR/genistein blends is discussed. There is a possible reaction between these two components due to their functional groups. In curing rubber, ENR is likely to be crosslinked by connecting the epoxide groups. The reaction was determined by both thermal method (DSC) and mechanical method (APA). Also a discussion on the melting points depression is included.

4.2 Experiment Section

ENR/genistein blends were prepared at 120°C for 9 min in a Brabender Plasticorder. To obtain morphology under a polarized optical microscope, solution
casting was applied to prepare the sample. The APA samples and DMA samples were made by compression molding at 150 °C under 20,000 pounds psi pressure for 30 min.

To discuss the thermal stability of the blends, we measured the decomposition points under a TGA system with nitrogen. DSC was used to understand thermal properties: the baseline shift demonstrates the glass transition, exothermic peaks might be related to curing reaction and endothermic peaks might represent melting process. The curing peak cannot be judged only from DSC results. APA was a method to determine the curing reaction from modulus as a complement for DSC. When we get the curing temperature, DSC may also be used to conduct the curing reaction in isothermal measurements. To supplement DSC results of glass transition temperatures, DMA was employed. From movement of tan delta we can probe the glass transition temperature shift

4.3 Results and Discussion

The following results demonstrated the thermal properties of ENR/genistein binary blends including decomposition points, glass transition temperatures, curing points and melting points.
4.3.1 TGA thermograms of ENR/genistein blends

Figure 4.1 TGA thermograms of ENR/genistein blends, indicating ENR could improve the thermal stability of genistein to some degree

Figure 4.1 shows the TGA plots for different concentrations of ENR/genistein blends superimposed on the same axis. The neat genistein starts to lose weight at first. There are two weight loss stages for genistein and the degradation still goes on even up to 600 °C. The first mass loss process might be due to the ring-opening in genistein structure causing vaporization of small molecules. The mass loss in pure ENR begins at 350 °C and ends at 450 °C. The degradation temperature increases with ENR component which means that ENR addition can improve genistein’s thermal stability to some degree. According to TGA results, we can not only get thermal stability of the binary blends but also set appropriate temperature for DSC runs.
4.3.2 Phase morphology of ENR/genistein blends

Figure 4.1 Phase morphology of ENR/genistein blends, showing crystals clearly at room temperature

The phase morphology of ENR/genistein at room temperature is shown clearly in Figure 4.2. The birefringent crystals can be seen in the dark background. Since ENR is non-crystalline polymer, the observed birefringent entity is presumably arising from the genistein crystal, although by no means conclusive. Hence, additional characterization methods need to be applied to identify these crystals.

4.3.3 Thermo behavior of ENR/genistein system before curing

Figure 4.2 DSC thermograms of ENR/genistein blends before curing from which glass transition, curing peaks and melting peaks can be observed.
From Figure 4.3, glass transition temperatures ($T_g$), curing temperatures and melting points of ENR/genistein system can be obtained. $T_g$ is around -20 °C which is the typical glass transition temperature of pure ENR 50, indicating that the two components in the blends can hardly react with each other in the Brabender processing. The exothermic peak around 250 °C may be attributed to the curing temperature as the crosslinking reaction is exothermic. This hypothesis would be supported by APA test later. Genistein, being a small molecule, does not show a $T_g$, but it has melting point due to its small crystalline molecule. The melting point of neat genistein is 302.9 °C and there is only one melting point which is close to pure genistein in each curve implying that no new crystal has formed in the blends. Hence, we may conclude that the crystal in Figure 4.2 belongs to genistein. However, from Figure 4.3, the melting temperature decreases with increasing ENR content except the ENR/genistein 20/80 concentration. The reason is that when ENR content gets higher, the distribution of genistein molecules are more dispersed, causing the distance between two genistein molecules longer which results in the greater intermolecular force. Thus, the melting point might have decreased due to the plasticization effect by ENR. With regard to the ENR/genistein 20/80 composition, small impurity can promote nucleation: the low ENR component helps provide formation of nuclei, which increases the melting temperature. There are no discernable melting points in ENR/genistein 70/30, 80/20, 90/10 compositions for two reasons: (1) as melting point decreases with ENR, the curing peak might overlap with the endothermic peak of crystal melting so that it cannot be determined unambiguously from the thermogram; (2) genistein might react with ENR completely without leaving any crystals above the curing peak.
However, we cannot conclude that the curing peak is actually 250 °C from the above thermograms as the scan rate of DSC was 10 °C/min, which was fast enough to affect the non-isothermal results apparently.

Figure 4.3 DSC thermograms of various heating rates implying that thermal lag is more obvious at higher scan rate and higher scan rate affords sharper peaks

Then we carried out the same blend at different scan rates, which is shown in Figure 4.4. The profiles in Figure 4.4 indicated that \( T_g \), curing peak and melting point are all dependent on the heating rate; the high heating rate results in higher glass transition temperatures, curing exothermic and melting endothermic temperatures, owing to the thermal lag. As the scan rate increases, there is insufficient time for the heat to conduct through the sample.[56] Therefore, the results in Figure 4.4 should be interpreted with reservation. The actual curing peak is more adjacent to 229.6 °C which was extrapolated from that at 2 °C/min. Also the melting temperature should be lower than 286.7 °C. Another distinction, which can be visualized from the thermogram, is that higher scan rate affords sharper peaks due to the higher sensitivity.
at the higher heating rate. Although the higher heating rate gives more pronounced peaks, we may miss important details if we run the test too fast.

Figure 4.4 Isothermal DSC thermograms of different temperatures showing that more pronounced peaks can be observed at high curing temperatures.

As is mentioned above, the curing peak around 250 °C is not the best one. To determine the optimum temperature for curing, isothermal scans of a specific concentration of ENR/genistein 50/50 were carried out from 220 °C to 280 °C for an hour at an interval of 10 °C. Figure 4.5 indicates that the higher the temperature, the more pronounced the exothermic peak becomes. There are no obvious exothermic changes in the 220 °C, 230 °C and 240 °C curves. If the reaction temperature gets higher, the reaction would be much more acute which would be in line with our expectation. However, the purpose of this research is to explore new plasticizer for PVC, and to stabilize PVC since it can easily decompose upon heating. That is to say,
curing temperature must be lower than the decomposition temperature of PVC. Also, high temperature is closer to the melting point of genistein. In this case, 250 °C seems to be the optimum temperature for curing reaction.

Figure 4.5Isothermal DSC thermograms of different compositions displaying the curing time is less than 10 mins

Now that the optimum temperature for curing has been identified, we can study in details for the curing process of each composition. Figure 4.6 depicts isothermal DSC thermograms as a function of concentrations. Pure ENR cannot cure by itself in 250 °C. With the addition of genistein gradually to ENR, the curing peak can be witnessed clearly. ENR/genistein 80/20 and 70/30 compositions revealed the highest exothermic peaks. From the time axis, one can infer that the curing time for each composition is less than 10 mins. In order to support this deduction, APA equipment is employed to test the curing time of blends at 250 °C.
Figure 4.6 APA results of ENR/G blends indicating each blend underwent a curing process and the curing time is less than 10 mins.

Table 4.1 Maximum storage torque & curing time of ENR/PVC blends

<table>
<thead>
<tr>
<th>Contents</th>
<th>Max $S'$ (dNm)</th>
<th>Time@90% cure (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ENR</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>ENR/G 80/20</td>
<td>8.379</td>
<td>9.8</td>
</tr>
<tr>
<td>ENR/G 60/40</td>
<td>8.999</td>
<td>5.6</td>
</tr>
<tr>
<td>ENR/G 40/60</td>
<td>11.713</td>
<td>4.62</td>
</tr>
<tr>
<td>ENR/G 30/70</td>
<td>15.545</td>
<td>3.6</td>
</tr>
</tbody>
</table>
Figure 4.7 gives the APA curves of ENR/genistein 100/0, 80/20, 60/40, 40/60 and 30/70 respectively. An oscillating strain rate was applied in the samples with the frequency of 1.67 Hz. The APA machine recorded both storage and loss torque amplitude when the sample was subjected to the oscillation shear at the temperature of 250°C. The abscissa (x axis) represents time and the ordinate (y axis) represents the storage torque amplitude which reflects the elasticity of the blends. The elevating of storage torque indicates high crosslinking density of the sample. If the curing process is finished, the torque curve will plateau out. The most valuable information we can get from the curve is T90, which is defined as the time to achieve the curing degree of 90%.\[57]\ T90 can be calculated in the following equation.

\[
T90 = \frac{90}{100}(M_H - M_L) + M_L
\]  \hspace{1cm} (4.1)

where \(M_H\) is the maximum torque and \(M_L\) is the minimum torque.

From Figure 4.7, each curve shows a crosslinking process except pure ENR which indicates pure ENR could not be self-crosslinked. The enlarged slopes demonstrate the curing rates for each blend. The slopes are nearly the same with different amounts of genistein. This phenomenon is probably because of the similar reaction kinetics between genistein and ENR.

Table 4.1 illustrates that the higher the genistein composition value, the higher maximum torque is and the shorter it takes to cure. Even the longest time of T90 is less than 10 minutes. The curing times for these four ENR/genistein compositions correspond to the ranges of curing peaks in Figure 4.6. The APA results also support that the exothermic change occurring in the vicinity of 250°C in Figure 4.3 must be the curing peak. After the curing process has finished, there is an obvious decline in the curves which implies that the crosslinked density starts to decline. This phenomenon can be interpreted as the breaking of crosslinked bonds.
4.3.4 Thermo behavior of ENR/genistein system after curing

After isothermal annealing, the blends completed the curing process. Then the thermal properties were analyzed again as shown in Figures 4.8 and 4.9.

![DSC thermograms of ENR/genistein 50/50 after curing showing stable melting temperature of genistein crystal](image)

**Figure 4.7** DSC thermo grams of ENR/genistein 50/50 after curing showing stable melting temperature of genistein crystal

![DSC thermograms of ENR/genistein blends after curing showing an increasing trend of T_g](image)

**Figure 4.8** DSC thermograms of ENR/genistein blends after curing showing an increasing trend of $T_g$
Figure 4.8 showed the effects of heating histories on the blends. The blend reaction underwent completely at 280°C as manifested by the lack of endothermic peak after curing. Judging from the relatively low melting point, there might be just a little genistein left after curing at 270°C. The results in these two temperatures suggested that higher temperature induces more conversion. But as temperature is restricted by PVC decomposition and genistein melting, we have to lower the processing temperature as much as possible. From Figure 4.8, one can also observe the elevation of $T_g$ with improving of isothermal temperature.

In Figure 4.9, the curing peaks disappeared as compared with Figure 4.2 while the melting points remained almost the same. The melting point of ENR/genistein 70/30 can be seen owing to the disappearance of curing peak. We concluded two plausible reasons for lack of the melting points mentioned before. As for ENR/genistein 70/30, the curing peak might be overlapped with the melting peak in Figure 4.3. In the case of ENR/genistein 80/20 and 90/10, genistein component reacted with ENR completely. With regards to the glass transition temperature, it is evident to discern the increasing trend changing from -21.8°C to 58.1°C in Figure 4.9, which indicates that the blends become more rigid upon curing. The DMA results (Figure 4.10) can also support systematic movement of the glass transition temperature after curing. The higher genistein amount, the higher glass transition temperature becomes. However, the maximum $T_g$ is still lower than that of PVC (80°C). It is reasonable to consider ENR/genistein cured system as plasticizer for PVC.
Figure 4.9 DMA results of ENR/G blends before and after curing displaying the $T_g$ movement
4.4 Conclusions

From the discussions above, it may be concluded that ENR and genistein can form miscible blends since genistein can cure ENR via the reaction between epoxide group of ENR and phenolic group of genistein. From TGA results, ENR can improve thermal stability of genistein a little bit. But the morphology at room temperature showed existence of crystal and the crystal proved to be genistein. The optimum curing temperature is 250 °C determined by conducting isothermal annealing at different temperatures. Before curing, the glass transition temperature of each concentration was around -20°C implying the immiscibility of these blends. But after curing, the blends displayed an elevation of $T_g$ and storage torque meaning high crosslinking density in the blends. Thus, genistein connected ENR into network. After curing, there is still some genistein left in the blends illustrating melting peaks in DSC curves. From the area under melting peaks, the residual amount of genistein can be calculated and the detail of calculation would be included in the next chapter. The depression of melting points can be interpreted by nucleation formation.
CHAPTER V

CALCULATION OF PHASE DIAGRAM OF ENR/GENISTEIN BLENDS

5.1 Introduction

Phase diagram is a graphical representation of physical states of substances under different conditions. From the phase diagram of polymer blends, we can obtain plenty of useful information to decide the suitable composition to meet requirements for applications. For instance, for a crystalline-amorphous blend, if we need the composition without crystal for use, we can search amorphous region in its phase diagram and determine the desired composition and temperature. Thus, phase diagram is a good guide to learn the states of polymer blends.

From the discussion above, genistein is the only stable crystal in the blends, and its melting points undergo the depression with addition of ENR. When we study the interaction in this binary system, there is a problem that curing reaction occurs before the melting behavior of genistein. The system is quite complex with a reaction involved as we should concern the exact stoichiometry and product in the reaction and the constituents are hard to determine. The problem can be simplified by considering the condition after curing. Genistein is regarded as the crystalline component and ENR, along with the product in the reaction is the amorphous constituent.

In this chapter, the phase diagram of ENR/genistein binary blends is constructed
based on the equilibrium theory for crystalline-amorphous blends developed by Matkar and Kyu[26]. From Chapter IV, we can get the experiment data of melting points of ENR/genistein blends after curing. Matlab is employed to simulate the phase diagram.

5.2 Experiment Section

The experiment data of melting points after curing come from Chapter IV which is obtained from DSC. The preparation of blends is described in Chapter III. The samples for DSC were prepared by melting method in a Brabender Plasticorder. The curing process was conducted in the DSC with a 60-minute isothermal step at 250°C. The melting points were measured after curing.

To obtain the heat of fusion of genistein, pure genistein underwent a melting process at various scan rates from 10 °C/min to 2 °C/min in DSC. Then extrapolation was applied to get the heat of fusion when the scan rate equals zero.

In this chapter, large amount of calculations are included. Although ENR and curing product are considered as a whole, the residual amount of genistein should be calculated by the heat of melting peaks. The calculation of $\chi_{ca}$ is described in equation 2.27. It is possible to draw the plot of $(1 - \frac{T_m}{T_0})$ vs $(1 - \phi)$ and to obtain the slope.

There are several variables in the equation of free energy. Some of them can be confirmed by experiment data whereas some should be deduced by the simulation model. The program for simulation was coded in Matlab.

To support the results of simulation, POM is used to observe the states of the blends. The samples of DSC cannot be used under optical microscope due to thickness. Therefore, the solution casting method was applied.
5.3 Results and Discussion

The results contain the determination of each parameter in the free energy equation. Some were deduced by experiment data and some were confirmed by fitting method.

5.3.1 Determination of compositions

Compared with a simple crystalline-amorphous system, curing reaction is involved in our system which alters the components after curing. When we construct the phase diagram, we cannot consider the compositions the same as we mix the blends. Both reagents face a reduction and new crosslinked product is formed. Although we ignore the curing reaction and just consider the condition after curing, the compositions should also be recalculated. It is very difficult to determine the extent of reaction due to the uncertainty and complication of crosslinked product. Then we treat ENR and cured product as one constituent and genistein as the other. The calculation of residual amount of genistein was conducted as follows:

From the DSC results, the heat of peak reflects the amount of materials. The amount of crystal could be attained from the area of melting peaks. However, as DSC peak is a result of all the possible thermal transitions, if we would like to calculate the crystal amount from endothermic peaks, we have to make sure the peaks are pure melting peaks without any other interference.
Figure 5.1 A typical DSC thermogram of pure genistein. Scan rate 10 °C /min. The enthalpy per gram of exothermic peak can be obtained from the peak area.

Figure 5.1 displays the endothermic peak of pure genistein. The onset starts at about 280°C which may be the combination of melting and decomposition process. Thus, the data calculated should be interpreted with reservation. The specific heat obtained by integration was 148.4 J/g with the scan rate of 10 °C /min for genistein crystal. Let’s take the composition ENR/genistein 30/70 for example. Figure 5.2 demonstrates the endothermic peak of ENR/genistein 30/70. Although Figure 4.1 shows the improvement of decomposition point of genistein with addition of ENR, there is still possibility that the endothermic peak may have degradation procedure involved. Therefore, the calculation of genistein amount has been simplified by not considering the decomposition effect.
Figure 5.2 A DSC thermogram of ENR/genistein 30/70. Scan rate 10 °C/min. The enthalpy per gram of exothermic peak can be obtained from the peak area.

The sample weight was 6.0000 mg and genistein took up 70% of the whole weight which means the weight of genistein in the sample was 4.2000 mg. If no genistein was consumed in the reaction, the heat of melting peak after curing should be 623.28 * 10^{-3} J. However, the actual ΔH for this composition after curing was 525.36 * 10^{-3} J. Thus, the conversion rate of genistein was 15.71% in this composition. According to the law of conservation of mass, the 15.71% weight of genistein had converted to the cured product. The fraction of residual genistein was 59.00% in the blend after curing. From Figure 4.9, a series of compositions can be calculated in this way. Table 5.1 lists the compositions and their corresponding melting temperatures.
Table 5.1 The compositions and their corresponding melting temperatures.

<table>
<thead>
<tr>
<th>ENR/G</th>
<th>Conversion proportion of genistein</th>
<th>Genistein left in blends after curing ($\phi$)</th>
<th>Melting point after curing (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/80</td>
<td>5.07%</td>
<td>75.94%</td>
<td>304.7</td>
</tr>
<tr>
<td>30/70</td>
<td>15.71%</td>
<td>59.00%</td>
<td>302.5</td>
</tr>
<tr>
<td>40/60</td>
<td>32.39%</td>
<td>40.57%</td>
<td>299.6</td>
</tr>
<tr>
<td>50/50</td>
<td>49.57%</td>
<td>25.22%</td>
<td>293.9</td>
</tr>
<tr>
<td>60/40</td>
<td>59.20%</td>
<td>16.32%</td>
<td>287.4</td>
</tr>
</tbody>
</table>

Figure 5.3 $T_m$ diagram of ENR/genistein blends showing the movement of liquidus line after curing
From the considerations above, it is possible to draw the $T_m$ diagram of ENR/genistein mixtures, which are demonstrated in Figure 5.3. It can be clearly seen that the liquidus line is shifted to amorphous rich region after the crosslinking is formed in the blends. The crosslinking probably reduces the plasticization effect of ENR on genistein which improves the melting temperature of genistein. Another possible reason is that the genistein connected to the ENR may have higher melting temperatures due to the increased molecular weight after curing.

5.3.2 Calculation of heat of fusion

The enthalpy of fusion $\Delta H_f$ is the change in enthalpy when heating a substance at a specific amount to make it melt. It is a latent heat which means the temperature is constant known as the melting temperature. The enthalpy of fusion data can be obtained in reference for most common substances. However, the data of genistein is not on the list of reference. Thus, we should consider measuring the heat of fusion of genistein by experiment. As the temperature should remain constant during melting, it is hard to achieve the complete melting process at a constant temperature in experimental condition. But an indirect approach can be taken into consideration. We can measure the heat of melting at various scan rates and use extrapolation to get $\Delta H_f$. Table 5.2 demonstrates the results at different scan rates.
Table 5.2 Heat of fusion at different scan rates.

<table>
<thead>
<tr>
<th>Scan rate (°C/min)</th>
<th>ΔH (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>148.4</td>
</tr>
<tr>
<td>5</td>
<td>120.5</td>
</tr>
<tr>
<td>3</td>
<td>130.3</td>
</tr>
<tr>
<td>2</td>
<td>113.7</td>
</tr>
</tbody>
</table>

Figure 5.4 shows the extrapolation method. The shown curve is fitted by method of least squares and is extrapolated to the y axes. The intercept is 109.76 J/g. The molar mass of genistein is 270 g/mol. Then we can get the molar heat of genistein by a multiply operation: \( \Delta H_m = 29635.2 \text{ J/mol} \).

Figure 5.4 The extrapolation method to get heat of fusion from intercept when scan rate is equal to 0
5.3.3 Determination of $\chi_{ca}$

Equation 2.27 has given the method of obtaining $\chi_{ca}$. In our system, genistein is a small molecule crystal which meets the requirement for validation of Equation 2.27. The melting points were available from DSC results in Figure 4.9 and the corresponding compositions were calculated in 5.3.1 (Table 5.3). Therefore, there is possibility to get the $\left(1 - \frac{T_m}{T_m^0}\right)$ vs $(1-\phi)$ points which is shown in Figure 5.5. The curve is fitted by method of least squares and it should meet the origin as the intercept equals zero in Equation 2.26. $T_m^0$ is the melting temperature of neat genistein (302.9 °C). As is displayed in the figure, the slope $B_c$ is 0.0413. Then, all the parameters on the right side of equation 2.27 are known. Then $\chi_{ca}$ for each composition can be determined.

<table>
<thead>
<tr>
<th>$1-\phi$</th>
<th>$1-(T_m/T_m^0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2406</td>
<td>0.010785</td>
</tr>
<tr>
<td>0.4100</td>
<td>0.014551</td>
</tr>
<tr>
<td>0.5943</td>
<td>0.019516</td>
</tr>
<tr>
<td>0.7478</td>
<td>0.029273</td>
</tr>
<tr>
<td>0.8368</td>
<td>0.040401</td>
</tr>
</tbody>
</table>
Figure 5.5 The melting point depression plot for the ENR/genistein blends. A linear slope was obtained by a least-square method from which the slope, $B_c = 0.0413$.

5.3.4 Effect of $r_1$ and $r_2$ on phase diagram

In the total free energy equation (Equation 2.21), $r_1$ and $r_2$ represent the numbers of statistical segments of each single component chain respectively. Regularly, the number of statistical segments is related to the molecular weight. When it comes to our system, genistein is no doubt a small molecule and the other constituent is a compound of ENR and cured product. The molar mass of uncured ENR can be determined but it is hard to confirm the molecular weight of cured product because of the crosslinked structure.

Figure 5.6 displays the effect on the choices of $r_1$ and $r_2$. For a regular solution, $r_1 = r_2=1$, and the UCST is a symmetric curve. For most blends, $r_1$ and $r_2$ are not equal. If we increase value of $r_2$, the critical concentration moves more and more toward high
concentration of crystal component showing asymmetry of UCST. For Figure 5.6 a) and b), all the parameters were the same except $r_1$. UCST moved upward with increasing of $r_1$ meaning that blends become less likely to form a homogeneous solution. Figure 5.6 a) and c) demonstrated the influence of $r_2$. With the increasing of $r_2$, the critical concentration shifted to right. $r_1$ and $r_2$ can play an important role in the position of UCST. According to Flory-Huggins theory, the segment length affects the interaction between molecules in the lattice model to influence the miscibility. However, the values of $r_1$ and $r_2$ did not affect the region of liquid-solid phase. Genistein is just a small molecule while the number of statistical segments for ENR and cured product is difficult to decide due to the mixture of uncured and cured polymer. But $r_2 > r_1$ can be sure. The better choice for the values of $r_1$ and $r_2$ is that $r_1=9$ and $r_2=60$. 
5.3.5 Effect of critical temperature on phase diagram

From 5.3.4, the critical temperature can be influenced by $r_2$. Figure 5.7 illustrates the phase diagrams with various critical temperatures. In Figure 5.7 a) and b), UCST was suppressed because of relatively lower critical temperatures. The blend undergoes liquid-liquid phase separation at lower temperature than the melting temperature of crystalline component. Generally speaking, the UCST started to affect solid-liquid transition, but not very obviously. In Figure 5.7 c), critical temperature improved and the UCST and the melting point depression curve intersected each other. The liquid-liquid coexistence interplayed with solid-liquid transition showing the region of
liquid + crystal (L +C). Among all the diagrams in Figure 5.7, Figure 5.7 d) was preferred due to the good fit of experiment data.

Figure 5.7 Effects of critical temperature on phase diagrams. High critical temperature makes UCST move upward indicating it is less likely to form a homogeneous solution.

From all the discussions above, a good fit of ENR/genistein phase diagram was able to be constructed (Figure 5.8). As

\[ \chi_{FH} = A + \frac{B}{T} \]  

(2.10)

and

\[ B = (\chi_c - A)T_{crit}. \]  

(2.11)

the entropic correction factor A was determined as -0.3 by fitting. It should be pointed out that the values of A, r1 and r2 and critical temperature just mainly influenced the amorphous-amorphous phase transition, but it hardly played a part in the
crystalline-amorphous phase transition. Other parameters were all obtained from experiment. In Figure 5.8, phase diagram was divided into three regions by interaction between solid-liquid phase transition and liquid-liquid phase transition. The solidus line was almost coincided with the pure genistein ordinate, which suggests that the amorphous constituent might be probably rejected from genistein crystals.

![Phase diagram of ENR/genistein blends](image)

Figure 5.8 Phase diagram of ENR/genistein blends which indicates three regions. The isotropic region can be used.

5.4 Conclusions

This chapter focuses on the construction of the crystalline-amorphous phase diagram. The parameters were determined either by experiment or fitting. The phase diagram was simulated based on Equation 2.21. The phase behavior of ENR/genistein blends is straightforward: when genistein crystal melts completely, the blend is isotropic at any concentration. When the temperature is below the melting point,
coexistence of crystal and liquid phase occupied most part of the phase diagram. Only small amount genistein can be dissolved in the amorphous component forming the isotropic phase. The solidus line almost coincided with pure genistein axis also supported that only limited genistein crystal can be accepted by amorphous constituent.
CHAPTER VI

DEVELOPMENT OF ENR/GENISTEIN BLENDS AS PLASTICIZER FOR PVC

6.1 Introduction

The properties of ENR/genistein binary blends have been discussed in the previous two chapters. The purpose of studying its blends with PVC is to achieve better performance of PVC material and to put into practice. In this chapter, ENR/genistein blends mixed with PVC hoping that it would be a good plasticizer for PVC. Firstly, to prove that ENR can improve the flexibility of PVC, ENR/PVC binary blends were characterized.

Genistein can act as curing agent and stabilizer for ENR/PVC system. However, due to the susceptibility of PVC to thermal decomposition, it degraded considerably in Brabender Plasticorder even in the presence of ENR and genistein. Although ENR and genistein can stabilize PVC to a certain extent, extra stabilizer is needed during mixing. We did not choose conventional stabilizer such as leads or barium-cadmium mixed metals. On one side, as this kind of stabilizer can work alone, it is hard to confirm the stabilizing effect of ENR and genistein. On the other hand, the objective of our research is to establish a novel plasticized system without any poisonous material. Thus, one reasonable choice is ESBO. Literature has reported that ESBO can stabilize PVC to some degree but cannot perform alone. Also, ESBO is a secondary stabilizer for PVC. To exclude the effect of plasticizing effect of ESBO,
ENR/PVC blends were considered first and the amount of ESBO was far below the required dose for plasticizing.

When evaluating the performance of the plasticized ENR/genistein/PVC/ESBO system, thermal properties and mechanical properties should be taken into consideration.

6.2 Experiment Section

ENR/PVC blends were first prepared by the solution casting method. The reason for abandoning the melting method was given in 6.3.1. ENR/genistein/PVC/ESBO blends were prepared by mixing these ingredients in the Brabender Plasticorder. As there were four components in the blends, the optimization of compositions is tedious. Table 6.1 demonstrates the fraction of each component. The principle for the choice of composition is that the ratio of ENR to genistein is 3:1 so that there will be little or no crystal left in the cured system. ESBO takes up 10% of the total amount of ENR and PVC. The ratio of ENR to PVC is variable as we need to explore the effect of ENR fraction. For pure PVC, it cannot be processed without or just with one stabilizer we chose before. Therefore, sample 1 contained 3.8% genistein of PVC. In this chapter, we signify the blends by ENR/PVC ratio instead of sample number for lucidity.
Table 6.1 The fraction of each component.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ENR</th>
<th>genistein</th>
<th>PVC</th>
<th>ESBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/100</td>
<td>0</td>
<td>3.7</td>
<td>96.3</td>
<td>10</td>
</tr>
<tr>
<td>10/90</td>
<td>9.7</td>
<td>3.2</td>
<td>87.1</td>
<td>10</td>
</tr>
<tr>
<td>20/80</td>
<td>18.7</td>
<td>6.2</td>
<td>75.1</td>
<td>10</td>
</tr>
<tr>
<td>30/70</td>
<td>27.3</td>
<td>9.1</td>
<td>63.6</td>
<td>10</td>
</tr>
<tr>
<td>40/60</td>
<td>35.3</td>
<td>11.8</td>
<td>52.9</td>
<td>10</td>
</tr>
<tr>
<td>50/50</td>
<td>42.9</td>
<td>42.9</td>
<td>14.2</td>
<td>10</td>
</tr>
<tr>
<td>60/40</td>
<td>50.0</td>
<td>33.3</td>
<td>16.7</td>
<td>10</td>
</tr>
<tr>
<td>80/20</td>
<td>63.1</td>
<td>15.8</td>
<td>21.1</td>
<td>10</td>
</tr>
<tr>
<td>100/0</td>
<td>75.0</td>
<td>25.0</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>

TGA was applied to measure the thermal stability. For pure PVC, air was purged instead of nitrogen to get suitable temperature for processing. DSC and DMA experiments were performed to determine the miscibility and movement of glass transition temperature. To grasp mechanical properties of blends, Instron was used to obtain strength-strain curves. Each sample has to be measured for at least three times to get the standard deviation.

Samples were compressed into films for DMA and Instron tests. The film forming process was carried out in a compression molding machine at the temperature of 150 °C under 50,000 psi pressure for 5 min.
6.3 Results and Discussion

The results of this chapter are divided into two parts: one is ENR/PVC binary blends by solution casting method and the other is ENR/genistein/PVC/ESBO blends by melting blending. Genistein and ESBO are stabilizers of PVC.

6.3.1 ENR/PVC binary blends

Figure 6.1 TGA result of PVC under air flow showing decomposition temperature that corresponds to about 95% consistent with literature

The TGA diagram of PVC was shown in Figure 4.11. It is seen that the decomposition point of PVC is 273.1°C in air. Then the melt-mixing method was put into practice to prepare ENR/PVC blends. But PVC turned brown even the processing temperature was 120°C, which is far away from the decomposition temperature of PVC. It implies PVC starts to degrade without weight loss before mixing well with ENR. Great difficulty was encountered to make ENR/PVC blends using the Brabender mixer. According to literature[45], stabilizer should be added in PVC prior to the
melt-blending. As stabilizer would bring additional factors that complicated the system, the melt-blending method was abandoned and instead the solution mixing approach is adopted here. There are two shortcomings with the solution casting method; one is that residual solvent can lower the glass transition temperatures as compared with that of the melt-blending approach; the other is that the blends would depend on the solvent type used, which would obstruct the practical application of the blends. Hitherto, all ENR/PVC binary blends were prepared by the solution casting method.

Figure 6.2 DSC thermo grams of ENR/PVC blends indicating good miscibility from single $T_g$. 

66
Figure 6.3 $T_g$ moving trend of ENR/PVC blends. ENR can plasticize PVC effectively by lowering the glass transition temperature.

As is shown in Figure 4.12 and Figure 4.13, there is only one single $T_g$ in each DSC thermogram curve of ENR/PVC blends. Moreover, the ENR/PVC system shows a systematic decrease of a single $T_g$ of ENR/PVC blend with increasing ENR content. This implies that ENR and PVC are miscible and with ENR added in PVC the blend can become a flexible system due to the plasticization effect to PVC. Compared with the experimental data in Figure 2.3 from the melt-mixing approach, the $T_g$ of each composition is lower caused by the residual solvent. In literature, the broadening of glass transition zone manifested above was attributed to the existence of structural inhomogeneity in the blends such as structural defects of PVC chains arising from different tacticity sequences such as head-to-head, tail-to-tail and head-to-tail. With
increased PVC amount in the blend, the effect of PVC gel particle becomes more pronounced, except that the glass transition zone becomes wider.

Figure 6.4 Variation of $T_g$ in ENR/PVC blends fitted with Fox Equation and Gordon-Taylor Equation

Figure 4.14 the scattered experimental $T_g$ points in comparison with the prediction by Fox Equation and Gordon-Taylor-Equation. The trend is similar to that of Figure 2.3, supporting that Gordon-Taylor Equation fits these points better than Fox Equation in the present ENR/PVC blend. In Matlab calculation, we choose the actual fitting parameter $k$ to be 0.2 in the Gordon-Taylor Equation. Thus, Gordon-Taylor Equation in this specific curve can be written as follows:

$$T_{gb} = \frac{T_{g1} + 0.2 T_{g2} W_2}{W_1 + 0.2 W_2}$$  \hspace{1cm} (6.1)

Then we can estimate $T_g$ for each concentration and choose the expected one.
6.3.2 Properties of plasticized system

The results above showed miscibility of ENR and PVC at all compositions. Here come the results of ENR/genistein mixing with PVC. ESBO served as additional stabilizer. Figure 6.5 displayed the thermal stability of ENR/genistein/PVC/ESBO blends. Neat PVC started to lose weight at about 220 °C. The addition of stabilizers improved the onset of degradation temperature of PVC a little bit, but not very much. The curing was not carried out at 250 °C for the blends containing PVC due to potential degradation. Therefore, in this chapter we only discussed the effect of uncured system on PVC.

Figure 6.5 TGA results of ENR/genistein/PVC/ESBO blends. With addition of ENR/G/ESBO, thermal stability of PVC improved a little bit.

Figure 6.6 showed DSC results of the blends. The glass transition temperature of each blend was displayed in Figure 6.7. For each blend, there was just a single glass transition point showing good miscibility of the four components blends. The glass
transition temperature shifted clearly and displayed the effect of plasticization the same as ENR/PVC blends. Meanwhile, the broadening of $T_g$ zone was still obvious in high concentration of PVC blends due to the structure of PVC.

Figure 6.6 DSC results of ENR/genistein/PVC/ESBO blends. Single $T_g$ indicates the four components blend mix well. Broadening of $T_g$ zone might be due to the structure characteristics of PVC.
Figure 6.7 T\textsubscript{g} movement of ENR/genistein/PVC/ESBO blends indicating good plasticization effect

DSC measured the T\textsubscript{g} from the change of heat flow during glass transition. To support the DSC results, DMA was employed to prove it in modulus. Figure 6.8 was the DMA results for the blends which indicated the glass transition temperature movement.
Figure 6.8 DMA results of ENR/genistein/PVC/ESBO blends indicating good miscibility and plasticization effect corresponding to the DSC results.
Figure 6.9 exhibits the stress-strain behavior of the blends. PVC containing genistein and ESBO stabilizers was very brittle and failed prematurely (see inset figure). With increasing ENR content to 10%, both Young’s modulus and yield strength improved greatly, but elongation at break is rather low, suggestive of brittle character. The tensile stress reached maximum with small amount of ENR. The more ENR was, the larger the tensile strain was.

![Graph showing stress-strain behavior](image)

Figure 6.9 Stress-strain behavior of ENR/PVC containing genistein in the fixed ratio of ENR:G 3:1 and the 10 wt% ESBO with respect to the total blend weight. The blends become more ductile with addition of ENR.

6.4 Conclusions

When it comes to the ENR/PVC blends, the notable trend of ENR/PVC blends is the relation of a single $T_g$ with a systematic movement indicating that ENR/PVC forms a single phase system. Nevertheless, there is a broadening in $T_g$ zone revealing possible heterogeneity in the blend owing to perturbing effect of PVC structure. The decreasing trend of $T_g$ with ENR content gives the possibility of making ENR an alternative plasticizer to toxic phthalates. ENR/PVC mixture is not a stable system.
and should be made only by solution casting method. Genistein is needed to realize the plasticization in practice. But only genistin was not enough. With addition of ESBO, a stable system was formed in the Brabender Plasticorder. Thermal stability of the blends was measured by TGA and the other three components can improve the stability of PVC a little bit. T_g measurement was conducted in DSC. Although there was an obvious reduction of T_g with amount of ENR, the T_g zone was still broadened with increasing of PVC as ENR/PVC blends. The trend of DMA results were the same as DSC results, demonstrating the success of the blends processing. To illustrate the mechanical properties, the tensile stress-tensile strain curves were obtained from Instron. PVC with stabilizers was quite brittle and almost had no mechanical properties. With the addition of ENR, the tensile strain and tensile stress improved.
CHAPTER VII

SUMMARY

In this thesis, the miscibility of ENR/genistein was discussed. Before curing, \( T_g \) of ENR/genistein blends remained constant at about -20°C and the melting point arising from genistein crystal is independent of the blend composition, suggestive of immiscible character. However, increasing trend of \( T_g \) of the blends is noticed after isothermal annealing the mixture which means genistein can cure ENR and form a miscible system. The phase diagram can be constructed from melting point depression after curing reaction. The simulation of phase diagram can guide us to choose reasonable region for application of ENR/genistein blends. ENR was proved to lower the glass transition temperature of PVC. To establish a stable system, genistein and ESBO was added in the blend. The blends showed good miscibility and can actually plasticize PVC. Furthermore, the blends displayed better mechanical properties compared with PVC with stabilizers.

The future work focuses on looking for a new way for ENR/genistein/PVC system to realize the curing reaction and develop a permanent plasticizer for PVC.
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