A Miscibility Study on Pullulan/Poly(Ethylene Glycol) Blends

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ABSTRACT

Miscibility of pullulan and poly(ethylene glycol) in aqueous solution has been determined by dilute solution viscometry. Blends of different compositions (100/0, 80/20, 50/50, 20/80, 0/100) with respect to pullulan/poly(ethylene glycol) have been prepared. Huggins plots of each homopolymer and polymer blend have been determined in aqueous solution at 25, 30 and 40 ^{0}C temperatures. From the data obtained from Huggins plots the miscibility parameters Δb, α, and μ have been calculated. The miscibility of polymers in a ternary system is measured by these parameters which are related to the slope of the Huggins's plot and the intrinsic viscosities of the polymers and the polymer mixtures. In addition to solution viscosity measurements, blend films were prepared by the solvent casting method and were tested by SEM and DSC analysis methods for the investigation of blend miscibility in the solid state. Moreover the molecular interactions between pullulan and PEG were studied by FTIR spectroscopy. Favorable interactions via H-bonding have been confirmed. The results have shown that pul/PEG blend with a blend composition of (80/20) is miscible in solution with positive miscibility parameter values for Δb, α, and μ respectively. DSC and SEM results indicate miscibility in the solid state as well.

Keywords: Viscosity, Miscibility, polymer blends, Pulluan, Poly(ethylene glycol)

ÖZ

Pululan (Pul) ve poli(etilen glikol) (PEG) polimerlerinin karışabilirliği seyreltik çözeltide viskometrik yöntemle tayin edildi. Pul/PEG bakımından 100/0, 80/20,50/50, 20/80, 0/100 kompozisyonlarına sahip beş değişik örnek hazırlanarak test edildi. Homopolimerlerin ve polimer karışımlarının Huggins eğrileri çizildi. Elde dilen veriden ΔB, μ ve α olarak tanımlanan karışabilirlik parametreleri hesaplandı. Karışabilirlik parametreleri Huggins eğrilerinden bulunan intrinzik viskozite ve Huggins sabitleri kullanılarak hesaplanmaktadır. Viskometrik ölçümlere ilaveten katı halde yapılan DSC, FTIR ve SEM analizleri için filmler hazırlandı. FTIR analizi iki polimer arasında hidrojen bağı etkileşimini doğrularken SEM ve DSC analizleri Pul/PEG 80/20 karışımının karışabilir olduğunu göstermiştir. Bu karışım için viskometrik ölçümlerden de pozitif ΔB, μ ve α değerleri elde edilmiştir. Buna karşılık Pul/PEG 20/80 karışımı için negatif karışabilirlik değerleri elde edilmiştir. Karışımdaki pululan oranı arttıkça Pul/PEG karışımı arasındaki karışabilirliğin de arttığı sonucuna varılmıştır.

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INTRODUCTION

Miscibility of polymers in dilute solution is of scientific interest and technological importance since it provides evidence on thermodynamic interactions between polymers, and gives clues on further industrial processing possibilities and applicability of the polymer mixtures.

Dilute solution viscometry is a practical and inexpensive tool to investigate polymer miscibility. Viscometric analysis of polymer-polymer miscibility in dilute solution is based upon the well known Huggins equation, which reflects the relationship between the specific viscosity η_{sp} and polymer concentration c, as follows:

$\eta_{sp} = [\eta]c+bc$

Where c is the concentration and $[\eta]$ is the intrinsic viscosity. While $[\eta]$ is a measure of the effective hydrodynamic volume of the isolated polymer, parameter b reflects the binary interactions between polymer segments. This is related to the Huggins coefficient k_H by the equation:

$\mathrm{b} = k_H \eta^2$

Miscibility of natural polymers with others is a currently investigated issue as exemplified by the studies carried on sodium alginate/pullulan [1], hydroxymethyl cellulose/pullulan [2] and dextran/pullulan [3] systems. Hence, the results of this thesis promise to contribute to the scientific literature.

This thesis work aims at studying miscibility of pullulan and poly(ethylene glycol) in dilute aqueous solution by viscometry. Both polymers are water soluble, Therefore dilute solution viscosity can be applied in aqueous solution. The method is useful to examine intermolecular interactions in solution. Moreover blend films with different ratios of Pul/PEG were prepared and studied by DSC and SEM techniques to compare results in solution and in the solid state. Understanding intermolecular interactions in Pul/PEG blends would serve in designing new systems for biomedical, pharmaceutical and other applications.

1.1 Polymer Blends

In the recent years, many efforts have been made to develop new polymer blends of natural polymers with each other or natural/synthetic polymer blends. The advantages of polymer blends are the ability to combine polymers with different properties,into new compositions with modified qualities. Other specific advantages of polymer blending are easy application and cheaper price. Therefore, this method can be have important role in technology and industry.

Definition of polymer blend is a mixture of at least two polymers or copolymers to create a new one with special emphasis on their mechanical behavior. The technology bring into existence many variation types of polymer blends from simple binary mixture to combination of homopolymers and copolymers, molecular composites, interpenetrating polymer networks (IPN), engineering polymer blends and many other systems. Therefore, types of polymer blends include elastomeric blends, impact modified polymers, liquid crystalline polymer blends, biodegradable polymer blends and block copolymer-homopolymer blends [4].

In most of the products that we use every day, we can see polymer blends. Some important synthetic polymer blends are poly(methyl methacrylate)/poly(vinylidine fluoride) PMMA/PVF$_2$ blends have better chemical and ultra-violet resistance than PMMA and PVF$_2$ alone. It has obvious applications in implant engineering. Additionally, PVF also exhibits improved elasticity and strength over polyester and polypropylene, two other polymers used for medical sutures [5].

A wide range of natural polymers evolved from renewable resources such as starch, cellulose and proteins. As biopolymers, starch and chitosan are two important candidates for use in bioplastics because of wide application range. Some of the most popular starch-based blend is together with PLA, PVA, and PEG. Glutaraldehyde has strong influence on the properties of pure starch, such as tensile strength and mechanical behavior. Chitosan has often been blended with popular polymers such as PSB (styrene-butadiene rubber), PCL (poly caprolactone), PLA (poly lactice acid), with appropriate properties than pure component. The applications of biopolymers are vast but the mainly of interest in the pharmaceutical and biomedical applications [6].

1.1.1 Compatibility and Miscibility

Miscibility and phase separation of polymer blends has long been studied for understanding the specific interactions between chemical structures. So, how chemical structure affects specific interactions in polymer blends is important in developing blending models and properties. A miscible polymer blend has a single-phase structure so it is a homogeneous polymer blend at a molecular level. Miscibility occurs if one glass transition temperature will be observed and thermodynamically negative value of the free energy of mixing is observed.

The immiscible blend is that made from two amorphous polymers and has two glass transition temperatures and show positive value of the free energy of mixing.

The phase behavior of polymer solution is a crucial property. Miscible polymer solutions often represent two solubility boundaries, the upper critical solution temperature (UCST) and the lower critical solution temperature (LCST). For blends with high molecular weight the existence of an LCST is more common than the (UCST), so that two substances are miscible at lower temperature.

The LCST depends on the polymer preparation, the monomer ratios and also the hydrophobic or hydrophilic nature of the polymer. Sometimes the opposite happens. Some polymer pairs exhibit an upper critical solution temperature (UCST) that is completely related to very small entropy of mixing. The positive entropy may cause miscibility but phase separation for some compositions at temperatures below the upper critical solution temperature (UCST). For example, triethylamine and water are miscible in all proportions below 19°C, but above this critical temperature, compositions separate into two phases. This means that ΔG is negative for the composition below 19°C and positive above this temperature [7].

A miscible mixture is compatible, although a compatible one is not necessarily miscible. A compatible blend is defined as "A polymer blend in which the component interact strongly with each other so that there is at least some miscibility. In highly compatible blends the components are fully miscible and the blend is in single phase" [8]

The criteria to distinguish between miscible, semi-miscible and immiscible blends are listed in Table 1.1.

Table 1.1. Properties and Behavior of Miscible, Semi-miscible and Immiscible Blends

Miscible Blends	Semi-miscible Blends	Immiscible Blends
Homogeneous	Homogeneous with trend phase separation	Heterogeneous with complete phase separation
Good mechanical properties	Good mechanical properties	poor mechanical properties
Excellent optical clarity	Good optical clarity	Poor optical clarity
one T_g value	Two Tg value	Two Tg value
$\Delta G < 0$	$\Delta G > 0$	$\Delta G > 0$
Stable	Metastable	Unstable
Compatible	Compatible	Incompatible

As the table above mentioned, the properties of polymer blends are determined mainly by the miscibility of the components and also compatibility be explained by thermodynamic stability of the mixture. Therefore a better understanding of polymer miscibility in solution and application of these blends also involved thermodynamic compatibility [9].

1.2 Thermodynamics of Miscibility

Thermodynamic interactions at the molecular leveland macroscopic parameters such as mixing are critical in controlling and modifying the processing, morphology, stability and mechanical properties of polymer blends. When two polymers are mixed with each other, several types of interaction may occur between the components. These interactions between molecules or segments are results of attractive forces between the components. So, strong or weak forces may be available in miscible mixtures. Some of important attractive interaction forces of miscible mixture are given in Table 1.2 [10].

Table 1.2. Types of Interactions Energy Forces in Mixture

Type of polymer	Type of interaction	Interaction Strength
"Non-polar" polymers	Physical	Weak
Weakly "polar" polymers	Physical	Weak
Strongly "polar" polymers	Physical-Chemical	Moderate
"Hydrogen bonded" polymers	Chemical	Moderate
Polymers that interact by formation of charge-transfer	Chemical	Strong
"Ionic" Hydrocarbon polymers containing ionic groups	Chemical	Strong

Understanding intermolecular forces can help us to explain miscibility of blends. Physical interactions are relatively weak interactions that cause dispersion forces. These types of forces are present between the nonpolar portions of the molecules. Ionic forces are the strongest intermolecular forces in the solution of the ionic substance; also Hydrogen bonding (type of dipole-dipole force) is the strongest intermolecular force in the solution of polar molecules. [9].

Negative Gibbs free energy is required for miscibility. Therefore, this value indicates that the solution process will occur spontaneously. Some of related equations are

$\Delta G_m = \Delta H_m - T\Delta S_m$ (1.1)

ΔS_m= entropy of mixing

ΔH_m= enthalpy of mixing

T = absolute temperature of the system

The positive heats of mixing (ΔH_m) are more usual and depend on solvent especially for non polar organic compounds.

For one-phase stability of binary system at constant temperature T and pressure P, with volume fraction of components ϕ are:

$$\Delta G_m < 0 \quad , \quad \partial^2 \Delta G_m / \partial \phi^2 > 0$$

1.2.1 Flory-Huggins Lattice Theory for Polymer Solution and Blends

Flory and Huggins introduced a lattice model of the thermodynamics of polymers in solution and blends in 1942. The concept of this model is calculating the changes of Gibbs free energy for mixing of polymer in a solvent. According to lattice model, each lattice expressed as a number of cells that occupied by arrangements of solvent or polymer segments. Three different ways of these arrangements are solvent-solvent, polymer-solvent and polymer-polymer [11].

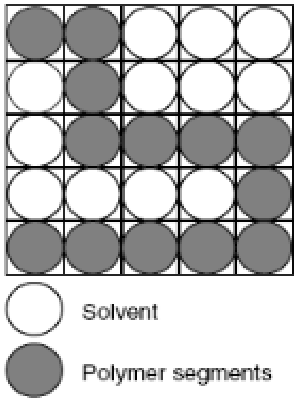


Figure 1.1. Schematic of solvent-polymer arrangements in a lattice of N cells

During mixing the volumes are not changing, so two terms of the entropic contribution is entirely related to the number of arrangement of polymer chain in solvent. The other terms are enthalpic contribution which is caused by interactions between segments when dissolved.

As a result of the number of possibile arrangements of the locations molecules, the small ones with the same size the total number of ways arrangements is given by:

$N=N_1+x\,N_2$

$N_{1=}$ the number of solvent molecules

N_2= the number of polymer molecules

x= each of segments

According to Boltzmann law, in a random mixing of two components the entropy of mixing, ΔS_m is given by [11]

$$\Delta S_m = -K[N_1 \ln (N_1/N) + N_2 \ln (xN_2/N) \quad (1.2)$$

Where ϕ_1 and ϕ_2 are volume fraction, thus

$\phi_1 = N_1/N$

$\phi_2 = xN_2/N$

So the equation (1.2) can be written as

$$\Delta S_m = -K(N_1 \ln \phi_1 + N_2 \ln \phi_2) \quad (1.3)$$

In equation (1.3), in an ideal solution, for a small solute each lattice position is occupied with one molecule, so x equals one. The volume fraction is defined as mole or molecular fraction. Since the entropy is positive, miscibility or immiscibility of the system mainly depends on the enthalpy of mixing value which is introduced by Flory-Huggins binary polymer-solvent interaction parameter, χ_{12}, so

$$\Delta H_m = KTN_1\phi_2 \chi_{12} \quad (1.4)$$

$X_{12} = z\Delta w/KT$

z = coordinate number of lattice

$\Delta w = w_{12} - 1/2\ (w_{11} + w_{22})$

Coordinate number determines how many solvent molecules can be surrounding a polymer; w_{11} and w_{22} are interactions energy between solvent-solvent and polymer-

polymer, also w_{12} is interaction of polymer-solvent which we described Δw as interchange energy. Combination of (1.3) and (1.4) can be expressed Free energy of mixing as thermodynamic terms

$$\Delta G_m = RT\,[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12}] \tag{1.5}$$

In this equation, we have n_1 and n_2 moles instead of N_1, N_2 molecules divided by Avogadro's number N_A for molar value.

The thermodynamics of Gibbs free energy of mixing in polymer blends is similar to polymer solutions, but they have differences between the strength of interactions in polymer blends compared to polymer with solvent. In solid polymers, intermolecular interactions increase and it will require more energy to break these interactions, therefore polymer blends are immiscible in the lack of any specific strength interaction between the components. Thus the most relevant equation for modeling the free energy of binary polymer mixtures is

$$\Delta G_m = RT\,[\phi_1/M_1 \ln \phi_1 + \phi_2/M_2 \ln \phi_2 + \chi'_{12}\, \phi_1\, \phi_2] \tag{1.6}$$

Where M_1 and M_2 are the degree of polymerization, and modified a equation regarding the polymer-polymer interaction parameter χ'_{12} between neighboring molecules. When Physical forces ($\chi'_{12}\phi_1\phi_2$) are unfavorable for miscibility and negative contribution of chemical forces ($\Delta G_m/RT$) are favorable for miscibility formation [12].

1.2.2 Solubility Parameter Approach

Miscibility can be estimated by another significant parameter which related the behavior of polymer chain in dispersion of the solvent. The compatibility between a polymer and a solvent determine the solubility of a polymer in some solvent. Thus, in a good solvent compatibility is high and in poor one we can see less interaction, hence compatibility is lower. As a result, polymer-polymer interaction solubility parameter written by Hildebrand is given in equation (1.7)

$$\chi'_{12} = V/RT\ (\delta_1 - \delta_2) \tag{1.7}$$

The solubility parameter (δ) is proposed especially for non-polar or weakly polar molecules representing cohesive energy density (CED)

$$\delta = (\mathrm{CED})^{1/2} = (\Delta H_v/V)^{1/2} \tag{1.8}$$

Where (ΔH_v) is molar energy of vaporization and (V) is per unit molar volume or actual molar volume, usually taken as 100 cm^3/mol. The values of ($\delta_1 - \delta_2$) will always be assigned zero or positive.

1.2.3 Binary Interaction Model of Polymer Blends

1.2.3.1 Intermolecular Repulsion Model

While Gibbs free energy of mixing was developed, some other various miscible systems have been found. Considering the case of homopolymer-copolymer or copolymer-copolymer blends as the mean field binary interaction model are prerequisite for obtaining miscibility as a result of repulsion effect between the units of copolymer. Usually copolymer in blends is random type which provides binary interaction parameter χ'_{12} positive value. Flory-Huggins expression for homopolymer-copolymer define as interaction parameter blend (χ_{blend}) as follows

$$\Delta G_m = RT\,[\phi_1/M_1 \ln \phi_1 + \phi_2/M_2 \ln \phi_2 + \chi_{\text{blend}}\,\phi_1\,\phi_2] \tag{1.9}$$

Consider a polymer blend of homopolymer 1 with monomer C, and copolymer 2 with A and B co-monomer, ϕ_A and ϕ_B are the volume fractions of copolymer unit can be written

$$\chi_{\text{blend}} = \phi_A\,\chi_{AC} + \phi_B\,\chi_{BC} - \phi_A\,\phi_B\,\chi_{AB} \tag{1.10}$$

The composition of poly(styrene-co-acrylonitrile)/poly(methyl methacrylate) (SAN/PMMA) is one of the intermolecular repulsion miscible of copolymer-homopolymer blends. Pure polystyrene and polyacrylonitrile are not miscible with homopolymer PMMA, but styrene-acrylonitrile (SAN) as copolymer mixing with PMMA is miscible [12].

1.2.3.2 Association Models

Association model has been proposed by Painter and Coleman described various range of synthetic polymer systems with strong specific interaction specially hydrogen bonding. This model has been applied for dextran first time [15]. The equation of association model has the main Flory-Huggins relation with added specific interaction by ($\Delta G_H/RT$) term

$$\Delta G_m = RT\,[\phi_1/M_1 \ln \phi_1 + \phi_2/M_2 \ln \phi_2 + \chi'_{12}\,\phi_1\,\phi_2] + (\Delta G_H/RT) \qquad (1.11)$$

Where (ΔG_H) is Gibbs free energy as result of changing in hydrogen bonding. This part of the equation describes the contribution of hydrogen bonding in the mixture and pure segment on free energy of mixing. The significant mixtures that are mentioned in Painter-Coleman equation are mixing self-associates component with another component does not self-associate which can form hydrogen bond with another component in pure state. Self-association occurs when one or both polymers have hydrogen bonding in pure state between the polymer chains. The main reason for describing this equation as strong interaction (O-H) is different contribution between composition and temperature compare to week interaction.

As an example for the application of this model imply poly(vinyl phenol) (PVPh) and poly(alkyl methacrylate) mixing, which (PVPh) is a self-associating polymer in pure state can form hydrogen bond, and poly(alkyl methacrylate) is non self-associating but it has a functional group that can react with hydrogen bonding with PVPh at 150 °C [13].

1.3 Preparation/Processing Methods of Blends

There are various techniques for preparation of polymer blends whose characteristics highly depend on the process of preparation. Since most of the polymer mixtures are immiscible and exhibit phase separation, proper method choice has an important role to achieve successful blending. There are a number approaches for preparation such as solution blending, latex mixing, dry mixing, interpenetrating polymer networks, melt mixing and precipitation. The simplest method is solution mixing which is the rapid method to evaluate phase separation by finding a proper solvent.

But sometimes this process can be misleading. The polymer-solvent interactions are less strong than polymer-polymer interactions and also it is essential to remove the solvent from blends. So this method is commonly used in laboratory scale for preparation of thin membranes and surface layers. Melt mixing, on the other hand, has a wide range of application because the well-defined components are mixed in molten state and polymer blends with strong mechanical properties are produced. Furthermore, this procedure is solvent-free and the mixing devices, for example, the same extruders (batch mixer) can be used for widespread polymer blends. For instance, thermoplastic blends are prepared by extrusion process. But consumption of high energy and uncontrolled chemical changing of components are drawbacks of melt mixing. At the end, to produce stable blends, miscible components should be mixed by slow diffusion rates [14].

1.4 Characterization by Instrumental Methods

Polymer blending is modified with optimized chemical, mechanical, biological and morphological properties and is characterized through spectroscopic and microscopic measurement. There are various methods that are sensitive to the composition of each phase of blends when each one has to be individually required to be characterized.

Thermal and thermo mechanical analyses are primary techniques that define miscibility of blends. Differential Scanning Calorimetry (DSC) is a thermo analytical method which determines glass transition temperature ($T_{g)}$. This method basically gives information on how phase transitions in blends change under heating. As polymer blends have high heat capacity, glass transition temperature occurs over the time. Immiscible blend exhibit two separate T_g values while single T_g is observed for miscible blends.

Scanning electron microscope (SEM) is a type of magnification electron microscope for surface analysis by focused on electron beams by producing images that easily recognize one or two phase regions of blend. Such features indicate morphological and compositional information that are valuable in miscibility study and applications.

Fourier transform infrared spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR) are spectroscopic methods which produce spectra for identifying advanced material properties. The goal of FTIR spectroscopy is distinguished how sample absorb monochromatic radiation at each wavelength. NMR spectroscopy is based on absorption magnetic field of isotope of the atoms. Furthermore, variations in chemical shifts in these techniques can provide evidence of specific intermolecular interaction. So these are powerful tools for characterization of structure of polymer blends [15].

1.5 Dilute solution Viscometry of Polymers

Viscosity of a polymer solution is defined as a resistance to flow which mainly depends on molecular weight of dissolved polymer. So the ability of a polymer solution to flow decreases with high molecular weight. Viscosity of liquids must be overcome to shear stress to keep the fluid moving. The shear stress is the force between macromolecules per unit area. If a liquid viscosity is less than that of water, it is called a mobile liquid. On the other hand, if a liquid viscosity is higher than water it is known as a viscous one.

A dilute polymer solution with concentration less than 1% indicate high viscosity compared to pure solvent or polymer solution with low concentration.

According to the laminar Newtonian flow, the basis for viscosity definition is Poiseuille’s equation under the steady-state condition which can be written as [16]

$$dV/dt = \pi r^4 P/8\eta l \tag{1.12}$$

V = Volume of liquid

t = Flow time

P = Pressure drop across the capillary

r and l = Radius and length of capillary

η = viscosity of fluid

In this equation we can find dynamic or absolute viscosity (η). So flow under the pressure through a vertical tube due to gravitational acceleration is

$$P = (h)g\rho \tag{1.13}$$

Where h is the average height of fluid column and ρ is the density of fluid. Therefore the Poiseuille’s equation is mainly related to time of fluid rearranged to

$$\eta = (\pi r^4 hg\rho t)/8lV \tag{1.14}$$

While viscometer and volume of all quantities are fixed, the equation (1.13) reduces to equation (1.15) in which A is a constant

$\eta = A\rho t$ (1.15)

The relative viscosity (η_r) is obtained simply by the viscosity of polymer solution divided by pure solvent.

$\eta = \eta/\eta_0 = \rho t/\rho_0 t_0$ (1.16)

Where t is flow time of solution and t_0 is flow time of solvent. Because of using dilute solution that is mainly related to flow time and the density of solution and solvent are almost the same $\rho = \rho_0$ we can neglect densities. The other quantity is specific viscosity (η_{sp}) that is measured by increasing viscosity due to polymer solution.

The next definition, reduced viscosity (η_{red}) is the most applicable kinetic amount related to polymer concentration. So, we may have got different reduced viscosity at each concentration. The intrinsic viscosity and inherent viscosity are the two other quantities that are reviewed in Table 1.3

Table 1.3. Nomenclature and Equation for Dilute Solution Viscosity

Nomenclature	IUPAC Name	Unit	Equation
Relative viscosity	viscosity ratio	dimensionless	$\eta = \eta/\eta 0 = t/t0$
Specific viscosity	–	dimensionless	$\eta sp = \eta_r - 1$
Reduced viscosity	viscosity number	dl/g	$\eta_{red} = \eta_{sp} / c$
Intrinsic viscosity	limiting viscosity number	dl/g	$[\eta] = \lim (\eta_{sp}/c)^{c\rightarrow 0}$
Inherent viscosity	Logarithmic viscosity number	dl/g	$\eta = \ln (\eta_r)/c$

Although dilute solution viscometry is not an absolute technique for characterization of polymer solution, it is popular, valuable, fast and inexpensive method that is experimentally simple. This method can measure accurately the molecular weight, so it is widely used for this important parameter as a routine measurement to definition of polymer performance.

1.5.1 Determination of Intrinsic Viscosity

A classical procedure to measure concentration of the solution viscosity can be formed as Taylor expansion [17]

$$\eta_r - 1 = \eta_{sp} = A_0 c + A_1 c^2 + A_2 c^3 + \dots \qquad (1.17)$$

Where the coefficient $A_0 = [\eta]$, indicate intrinsic viscosity which dividing by concentration (η_{sp}/c) gives Huggins equation. A plot of (η_{sp}/c) versus concentration shows straight line and is measured by extrapolation of (η_{sp}/c) to zero concentration. The Huggins equation written in form of

$$\eta_{sp}/c = [\eta] + k_H [\eta]^2 c \tag{1.18}$$

k_H = Huggins constant, dimensionless, generally ranges between 0.35 in good solvent and 0.5 in poor solvent.

Thus $[\eta]$ obtained as intercept of linear plot. Alternatively, intrinsic viscosity can be calculated by linear plot ($\ln \eta_r/c$), that is called inherent viscosity, versus concentration of polymer. So explained by the Kraemer equation

$$\ln \eta_r/c = [\eta] - k_K [\eta]^2 c \tag{1.19}$$

k_K = Kraemer constant, generally negative and around –0.15[2]

The relationship between both coefficient of k_H and k_K is shown by equation (1.20) which this condition is following for flexible coil.

$$k_H + k_K = 0.5 \tag{1.20}$$

To identity of terms (1.17) and (1.18), expanding $\ln \eta_r/c$ in terms of η_{sp}/c related to intrinsic viscosity yields

$$\ln \eta_r/c = (\eta_{sp}/c) - (\eta_{sp}/c)^2 (c/2) + (\eta_{sp}/c)^3 (c^2/3) + \dots \tag{1.21}$$

Which the equation (1.21) follows that to explain

$$\lim (\ln \eta_r/c)_{c\to 0} = \lim (\eta_{sp}/c)_{c\to 0} = [\eta] \qquad (1.22)$$

According to Huggins and Kraemer equations, however the plot of (η_{sp}/c) and (ln η_r/c) will both extrapolate to [η] at zero concentration and are linear. But the slopes of them will have different values; one has positive slope and another one negative. Measuring of intrinsic viscosity is an important value for measuring the molecular weight. Schematic diagram of typical Huggins-Kraemer plot is shown in Figure 1.2.

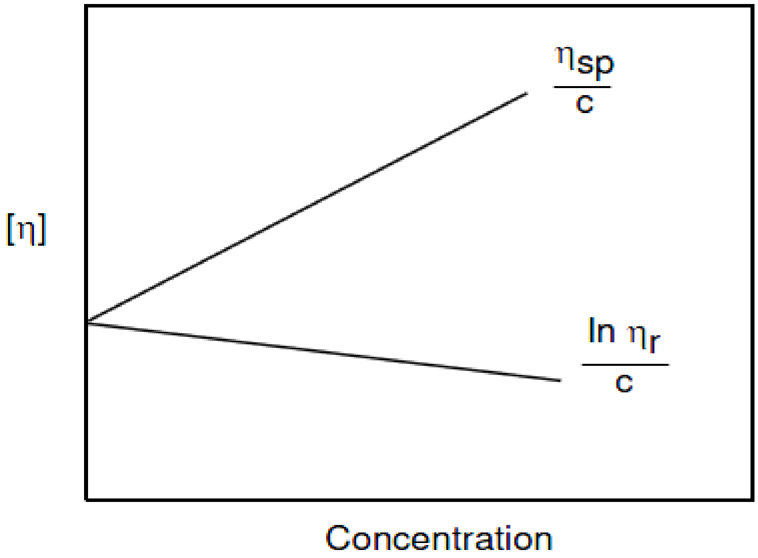


Figure 1.2. Typical Huggins and Kraemer Plots

1.5.2 Correlation of Intrinsic Viscosity and Molecular Weight

As mentioned before, viscosity of polymer solution mainly depends on concentration and molecular weight of dissolved polymer. Since all polymers increase the viscosity of solvent, make this method as a proper approach to determine molecular weight. The other polymer physical properties also increase, such as impact resistance, elasticity, phase behavior with increasing molecular weight. We are actually describing Mark-Houwink equation which indicates relation between intrinsic viscosity [η] and molecular weight M, so

$$[\eta] = KM^{\alpha} \tag{1.23}$$

Where both K and α, are the Mark-Houwink constants that depends on the type of polymer-solvent and also on temperature. Log [η] plot of versus log M yield a straight line with intercept log K and slope α. The exponent α is typically between 0.5 (for a theta solvent) and 0.8 (for a good solvent). Actually stiff molecules of polymer with a long chain exhibit high values of α constant with good solvents around the range of 1 <α> 1.7. Higher theoretical value of around 2 is observed for rigid rods of polymers. In addition, intrinsic viscosity is higher for these polymers. In theta solvents, which are free from energies of solvent-solvent interactions, with flexible chain segments of polymer attract each other strongly compared to solvent molecules. So, the solution exhibits lower intrinsic viscosity value and the exponent of α is closed 0.5. As a result, the logarithmic plot of [η] vs M should be linear over a given molecular weight [2].

1.5.3 Dilute Solution Viscometry and Its Relation to Compatibility Studies

The compatibility of polymers in solution can be analyzed accurately by viscosity techniques. Compatibility of a polymer-polymer-solvent ternary system can be estimated by measuring the intrinsic viscosity values. According to Huggins equation, the empirical relation between specific viscosity η_{sp} and concentration of polymer is expressed as [18][19]

$$\eta_{sp}/c = [\eta] + k\,[\eta]^2\,c \qquad \text{(I.24)}$$

Where η_{sp} is specific viscosity as single-solute in this equation, the plot of η_{sp}/c versus c yields linear plot with intercept $[\eta]$ and also the slope is binary interaction between polymer segment, b, which is related to Huggins constant k by equation $b = k_H\,[\eta]^2$.

If we put constant b in Huggins equation (1.24), we can write

$$\eta_{sp}/c = [\eta] + bc \qquad (1.25)$$

Values of b and $[\eta]$ can indicate miscibility of the polymer 1 and polymer 2.

In order to estimate the miscibility or immiscibility of polymer blends, Chee proposed an ideal expression for interaction parameter ΔB and μ, when polymers are mixed in weight fractions of component w_1 and w_2 as

$$\Delta B = b - b^{-} / 2\, w_1 w_2 \qquad (1.26)$$

According to this equation, the coefficient b and b^{-} given by

$$b = w_1^{\,2}\, b_{11} + w_2^{\,2}\, b_{22} + 2\, w_1\, w_2\, b_{12} \qquad (1.27)$$

$$b^{-} = w_1b_{11} + w_2b_{22} \tag{1.28}$$

Using these values, a more effective parameter μ can be defined as follows:

$$\mu = \Delta B/\{[\eta]_2-[\eta]_1\}^2 \tag{1.29}$$

Where μ is Chee’s interaction parameter, $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. The polymer blend is miscible while $\mu \geq 0$ and $\mu < 0$ indicate phase separation.

Sun et al has proposed another miscibility criterion, α, for determination of polymer-polymer miscibility in the absence of strong specific interaction between macromolecules that cause aggregation and also in low concentration as [20]

$$\alpha = K_m - (K_1w_1^2[\eta]_1^2 + K_2w_2^2[\eta]_2^{\,2} + 2\,(K_1\,K_2)^{½}[\eta]_1[\eta]_2\,w_1\,w_2\,)/\{[\eta]_1w_1 + [\eta]_2w_2\}^2 \tag{1.31}$$

Where K_m, K_1 and K_2 are Huggin’s constant for mixture, component 1 and component 2 and α is the Sun interaction parameter, for ternary mixture (polymer 1-polymer 2-solvent).

The sign of parameter α predicts miscibility of polymer blends, when $\alpha \geq 0$ miscible. For values of $\alpha < 0$ the blend is regarded as immiscible.

For ternary systems, three types of interaction contribute to evaluation of K_m, such as [20] [22]

1. Long range hydrodynamic interaction of pairs of single molecules, defined by K_{m1} which is equal to K_m interaction parameter of blend ($b = k [\eta]^2$)
2. Double molecules formation given by K_{m2}

   $K_{m2} = ([\eta]_2 - [\eta]_1)\, k / [\eta]^2$
3. Intermolecular attraction or repulsion as K_{m3} which is equal α, ($K_{m3} = \alpha$)

Therefore the sum up of this parameter in order to K_m written by [21]

$$K_m = K_{m1} + K_{m2} + K_{m3} \tag{1.31}$$

As mentioned before, in the absence of strong specific interaction and low concentration in non-polar solvent, the terms K_{m2} can be neglected, so equation (1.31) rearranged in order to reabbreviating K_{m3} as α to equation (1.32)

$$\alpha = K_m - K_{m1} \tag{1.32}$$

In general, if ΔB, μ, and α are positive for any polymer blend it indicates miscibility, whereas if these values are negative phase separation is presume. For coefficient α, if there are attractive interaction among molecules stronger than hydrodynamic one $\alpha > 0$, on the other hand if the interactions are repulsive $\alpha < 0$ and while $\alpha = 0$ exhibit the miscibility region.

A completely empirical equation for measuring an ideal behavior of solution described by Krigbaum and Wall parameter Δb, which adapted by the Huggin's equation (1.24) set a new formula as [23]

$$\eta_{sp,m} = [\eta]_1 c_1 + [\eta]_2 c_2 + b_{11}c_1^2 + b_{22}c_2^2 + 2b_{12} c_1c_2 \qquad (1.33)$$

Where $\eta_{sp,m}$ the specific viscosity of mixing polymer (subscript m abbreviated as mixing), $[\eta_1]$ and $[\eta_2]$ are the intrinsic viscosity of component 1 and 2, c_1 and c_2 are the concentration of mixing respectively, and b_{12} express the interaction coefficient for the mixture of 1 and 2 components, then

$$(b_{12})_{exp} = \eta_{sp,m} - [\eta]_1 c_1 - [\eta]_2 c_2 - b_{11}c_1^2 - b_{22}c_2^2 / 2c_1 c_2 \qquad (1.34)$$

$$(b_{12})_{theo} = (b_{11} b_{22})^{½} \qquad (1.35)$$

Because of the definition of interaction coefficient polymer blend, $b_{12,}$ are not acceptable for system with negative slopes, therefore b_{11} and b_{22} are modified in equation (1.35) by Williamson and Wright theoretically as

$$(b_{12})_{theo} = (b_{11} + b_{22}) / 2 \qquad (1.36)$$

Comparison of experimental b_{12} and theoretical values, give us some information about interaction between polymer 1 and 2, so compatibility of polymer mixture is characterized by Δb parameter

$$\Delta b = (b_{12})_{exp} - (b_{12})_{theo} \tag{1.37}$$

As a result, negative values of Δb indicate incompatibility of solutions systems, whereas polymer solutions are compatible while Δb has positive values with attractive interactions.

1.6 Pullulan and Poly(ethylene glycol)

1.6.1 Pullulan

Pullulan is produced by polymorphic fungus Aureobasidium pullulans which is structurally described as repeating linear glucan units consisting α-(1→4) linked to other series units as α-(1→6) bonds that creating long chain structure. [α-D-Glc$_p$-(1→4)-α-D-Glc$_p$-(1→4)-α-D-Glc$_p$-(1→6)]$_n$

The monomer formula is ($C_6 H_{10} O_5$) which is produces with different weight-average molecular weight with the range of around 100,000-200,000 kDa. Industrially pullulan is produced by fermentation process of starch under controlled modification non-toxigenic and non-pathogenic strain on Aureobasidium pullulans Figure 1.3 [23].

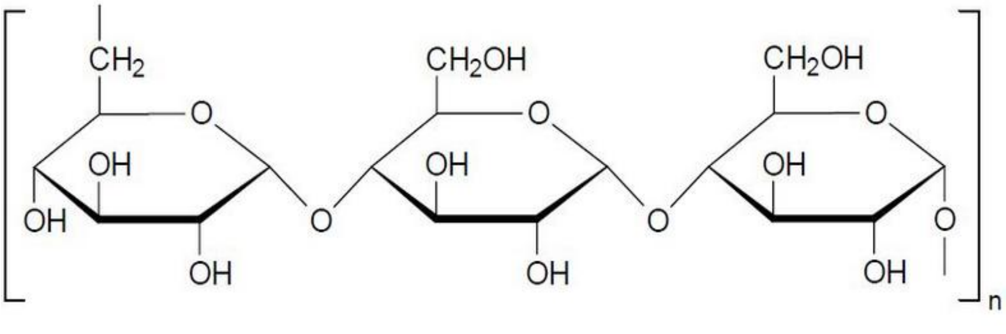


Figure 1.3. Chemical Structure of Repeating Linkage of Pullulan

Pullulan is water-soluble and resistant to change in viscosity with changing in temperature and pH. Also it is chemically modified to another derivative with low solubility or completely insoluble in water. In addition, it is an excellent film forming agent and adhesive which is used in drug delivery with good oxygen barrier properties as a carrier in the preparation of capsules, coating for tablets. Pullulan has "Generally Regarded As Safe" (GRAS) status for a wide range of applications and used as food ingredient. Physical properties and some characteristics of pullulan are summarized in Table 1.4 [24].

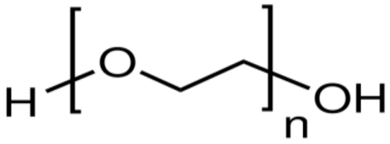
Table 1.4. Physical Properties and Characterization of Pullulan

Solubility	High solubility in water, not soluble in organic solvents, soluble mainly in ethanol, substitution with ether and ester make pullulan insoluble in water and soluble in organic solvent
pH	5.0 - 7.0
Appearance and properties	Dry white powder, tasteless and odorless, non-toxic, edible
Viscosity	Stable viscous solution, low viscosity compare to other polysaccharides
Film forming	Low oxygen permeability, thermally stable, dissolve fast in water
Biodegradability	Degraded by microbial enzymes, pullulan and isopullulan fermented to short chain fatty acids by bacteria, degradation faster than other dextran
Moisture Retention	10-15% moisture content
Adhesiveness	Intensively adhesive, adheres to foods

Due to pullulan's properties and also chemical modification, it has wide range of applications and is used in many fields like tissue engineering, pharmaceutical and drug delivery and food science [25].

1.6.2 Poly(Ethylene Glycol)

Poly(ethylene glycol)(PEG) or poly(ethylene oxide)(PEO) ,the two names of polymer which are chemically same but PEG with a molecular mass below 20,000 g/mol, PEO with a molecular mass above 20,000 g/mol. It is a biodegradable, hydrophilic polymer which is soluble in water, and many organic solvents like methanol, benzene it is insoluble in hexane. It has a pH of 5-7in water. It has a repeating unit of $H(OCH_2CH_2)n$ OH



It has low-toxicity, and is odorless. It evaporates hard and has highly flexibility which is useful for surface treatment applications. PEG is used in many fields like medical, industrial, cosmetics, metal working, electronics and pharmaceutical uses. These applications are based on water solubility, thermo plasticity and flocculation ability. Due to low-toxicity PEG is used as food additives, as surfactants, components of pharmaceuticals to improve drug solubility. It is also used as drug carriers, as biocompatible surface coatings and as tablet binders. For industrial uses PEG is an excellent agent in agricultural products, brighteners electroplating, detergents and cleaners with low volatility, and in ceramics manufacture. As a result, most of the properties of this material depend on molecular weight that means different molecular weights find use in different applications [26].

Chapter 2

EXPERIMENTAL

2.1 Chemical Materials and Their Purification

Pullulan, a product of Freda Biotechnology Co.Ltd (China) is a white powder sample with molar mass 1.10×10^5 Da found by dilute solution viscometry. It was used as received without further purification.

Poly(ethylene glycol) is product of Aldrich co.ltd-Gillingham UK . It has molecular weight of M_n=8000 and density of 1.027g/cm^3 and was used without further purification.

Water: Double distilled water was used as solvent.

2.2 Apparatus

Viscometer: Ubbelhode type glass viscometer was used for dilute solution viscosity measurement at different temperatures.

Figure 1.4. Ubbelohde Viscometer

Water bath and Heater: Viscosity measurement was carried out in constant temperature water bath in which temperature was kept constant within range 0.1°C sensitivity by an electrically controlled thermostat.

Filtration Apparatus: Aldrich S & S PTFE (Teflon) membrane filters with 0.45 µm maximum pore size were used together with syringe-mountable filter holders with diameters of 25mm were used.

Others: Stop watches for time measuring, sensitive thermometers (±0.1 °C) for maintaining a constant temperature.

2.3 METHOD

2.3.1 Viscosity Measurement

Both homopolymers and polymer blends of Pul/PEG were studied by dilute solution viscometry in distilled water at 25, 30 and 40 ^{o}C. Stock solutions of each binary and ternary system were prepared at room temperature by stirring the mixture for 45 minutes. The concentration of the stock solution of Pul/PEG was (2% w/v). Blend samples with composition of Pul/PEG (100/0, 80/20, 50/50, 20/80 and 0/100) were prepared with an initial concentration of 2% w/v. Temperature was fixed in a thermostat bath with thermal stability of ±0.05 at 25, 30, 40 °C. Average flow times of each sample of polymer blends with different concentrations were studied by using Ubbelohde viscometer. The intrinsic viscosity and the linear plots of these values versus concentration were obtained.

2.3.2 Film Preparation

Thin films of Pullulan, PEG and Pul/PEG samples were prepared by the solvent evaporation method. Aqueous solution of 2% (w/v) polymers and their blends dried at 50 ^{0}C for preparing for FTIR spectra and for SEM and DSC analyses.

.2.3.3 Calculations

2.3.3.1 Intrinsic Viscosity and Huggins Coefficient Calculations

Intrinsic viscosity of various compositions pul/PEG blends and also Huggins coefficient values were calculated by equations given in section 1.5.1 and 1.5.3.

2.3.3.2 Miscibility Parameter

Miscibility parameters ΔB, μ, α were calculated according to equations given in section 1.5.3.

2.3.4. SEM Analysis

SEM analysis was carried out in TUBITAK-MAM, Gebze using a JEOL 840JXA SEM (equipped with EDS system for microanalysis) instrument.

2.3.5 FTIR Analysis

Fourier-Transform IR Spectrometer obtained films were recorded on a Perkin Elmer Spectrum Two^{TM} FT-IR spectrometer equipped with WINFIRST software.

2.3.6 DSC Analysis

Perkin Elmer Diamond differential scanning calorimeter was used to perform differential scanning calorimeter (DSC) measurements for Pullulan film and Pul/PEG film samples. The measurment was done by Merkez Laboratuvar –Middle East Technical University in Ankara, under a nitrogen atmosphere at a constant heating rate of 10^{o}C/min.

Chapter 3

Results and Discussion

3.1 The Viscosity Studies of Pullulan and Poly(ethylene glycol) Solutions and Blends

Dilute solution viscometry was carried out to find out the miscibility window for different blends of Pul/PEG of compositions (100/0, 80/20, 50/50, 20/80 and 0/100) at 25, 30 and 40 ^{0}C. The molecular weight of pullulan is not provided by the manufacturer. Therefore, the viscometric data obtained at 25 ^{0}C was used to calculate the viscosity average molecular weight of pullulan taking K and α values as 2.21×10^4 (dl/g) and 0.66 respectively as reported in Table 3.1 [25]. The parameters used to calculate the molecular weight of pullulan are given in Table 3.1, and the Huggings plot is given in Figure 3.1. The plot of $[\eta_{sp}/c]$ versus concentration gives $[\eta]$ as intercept are shown in Figure 3.1.

As a result, the intrinsic viscosity is obtained 0.4717(dL/g) and the molecular weight according to equation (I.23) was calculated ($M_w = 1.11 \times 10^5$ Da).

Table 3.1. Viscosity Data for Pullulan at 25 ^{0}C

Sample	W_{pul}	$[\eta]$ (dl/g)	b	R	$K \times 10^4$ (dl/g)	α
Pullulan	0.4051	0.4717	0.0523	0.99	2.21	0.66

Where $[\eta] = KM^{\alpha}$

Figure 3.1 show the reduced viscosity versus total concentration at 25 ^{0}C.

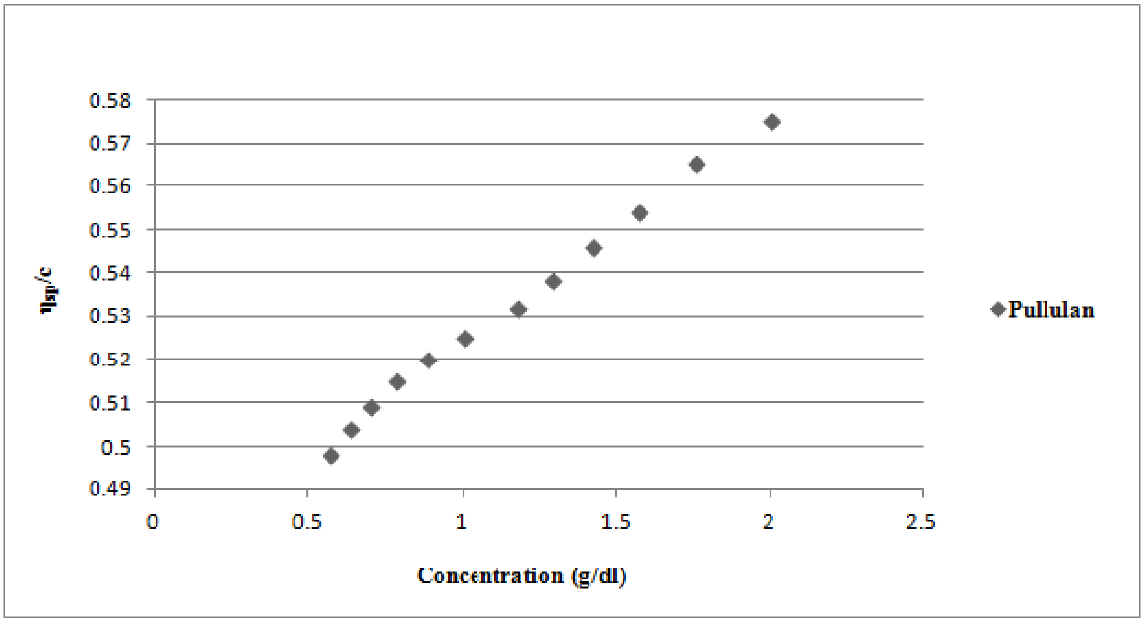


Figure 3.1. Reduced Viscosity vs Total Concentration of Pullulan at 25 ^{0}C

The viscosity data for pullulan, PEG and Pul/PEG blends are given in Tables 3.2, 3 and 4 respectively. The Huggins coefficient k_H and interaction parameter b as slope for each polymer have been calculated using the Huggins plots (η_{sp}/c) shown in Figure 3.2, 3 and 4. Linear relationships are observed for pure pullulan, pure PEG and for all compositions of blends. The intrinsic viscosity of pullulan is greater than intrinsic viscosity of PEG since PEG used in this study is an oligomer of 8000 Da molecular weight. In addition, the intrinsic viscosities of both polymers and their blends decrease with increasing temperature because with increasing the temperature the resistance to flow is reduced. As the fraction of PEG is increased in the mixture the intrinsic viscosity takes lower values. The conformations of polymers could be predicted from the Huggins coefficient k_H. The Huggins coefficient can take values in the range 0.2-0.8 for flexible polymer chains. Usually this value is around 0.5 in θ-solvents and near 0.3 in good solvents for flexible random coil polymers. At all temperatures studied the Huggins coefficient values of all samples have been found to be in the range 0.2-0.4 so the polymer systems studied have random coil conformations.

Table 3.2**.** Viscosity Data for Pullulan, PEG and Pul/PEG Blends at 25 ^{0}C

Sample	W_{pul}	[η] (dL/g)	b	k_H	R
Pullulan	0.4051	0.469	0.0533	0.24	0.99
Pul/PEG 80/20	0.3044	0.403	0.0586	0.36	0.99
Pul/PEG 50/50	0.2032	0.367	0.0368	0.27	0.99
Pul/PEG 20/80	0.1041	0.313	0.0201	0.21	0.98
PEG	0	0.262	0.0144	0.21	0.97

Table 3.3**.** Viscosity Data for Pullulan, PEG and Pul/PEG Blends at 30 ^{0}C

Sample	W_{pul}	[η] (dL/g)	b	k_H	R
Pullulan	0.4043	0.436	0.0536	0.28	0.99
Pul/PEG 80/20	0.3025	0.375	0.0580	0.41	0.99
Pul/PEG 50/50	0.2054	0.338	0.0363	0.31	0.99
Pul/PEG 20/80	0.1038	0.286	0.0223	0.27	0.98
PEG	0	0.238	0.0150	0.27	0.97

Table 3.4. Viscosity Data for Pullulan, PEG and Pul/PEG Blends at 40 ^{0}C

Sample	W_{pul}	[η] (dL/g)	b	k_H	R
Pullulan	0.4041	0.405	0.0543	0.33	0.99
Pul/PEG 80/20	0.3036	0.347	0.0586	0.48	0.99
Pul/PEG 50/50	0.2044	0.304	0.0398	0.42	0.99
Pul/PEG 20/80	0.1053	0.259	0.0214	0.31	0.98
PEG	0	0.213	0.0145	0.31	0.97

Where $b = k_H [\eta]^2$

Figures 3.2, 3 and 4 are shown the reduced viscosity versus total concentration of polymers and their blends in solution at 25, 30 and 40 ^{0}C.

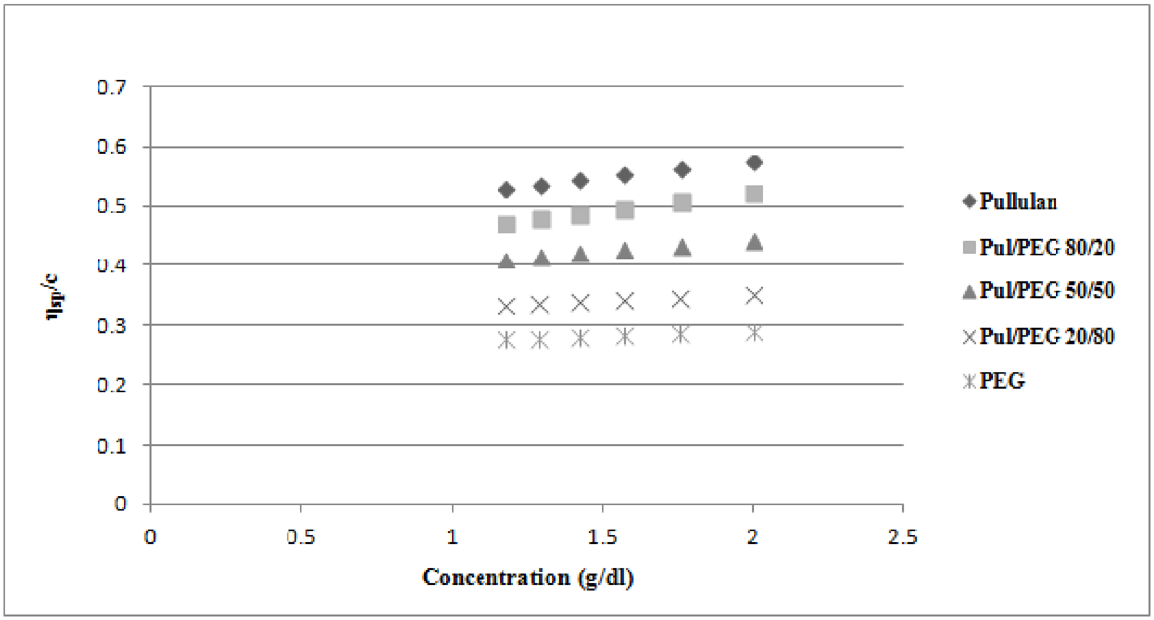


Figure 3.2. Reduced Viscosity vs Total Concentration of Polymers at 25 ^{0}C

As can be observed in Figures 3.2, 3 and 4, reduced viscosity against concentration plots for polymer blends samples are linear plots and the correlation coefficient, R, values are near to unity as given in table.

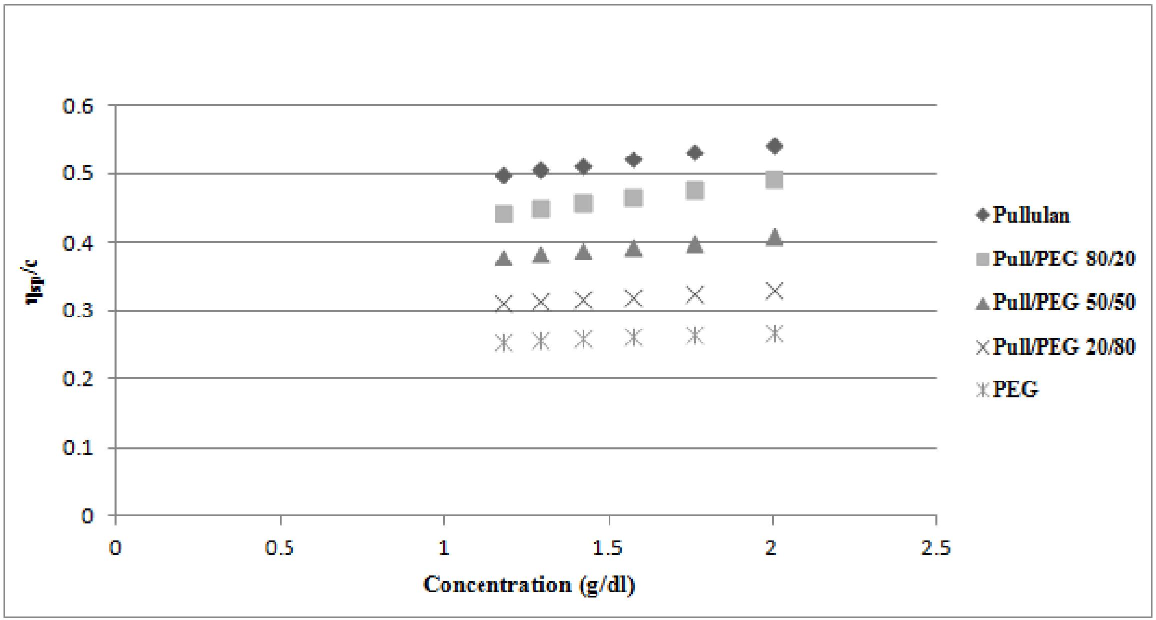


Figure 3.3. Reduced Viscosity vs Total Concentration of Polymers at 30 ^{0}C

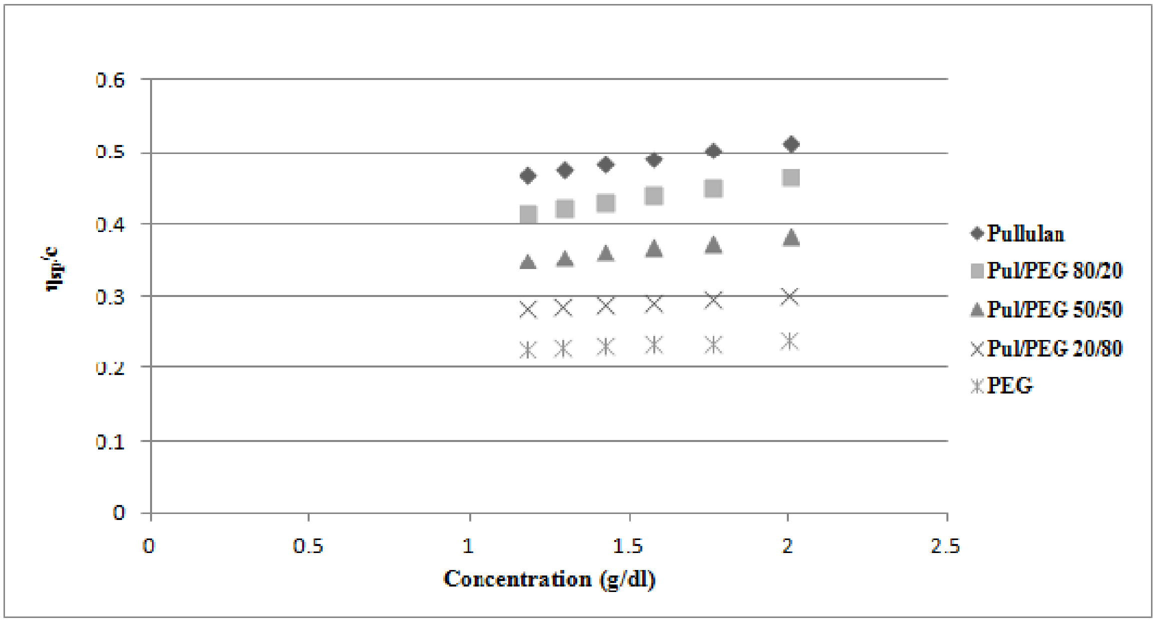


Figure 3.4. Reduced Viscosity vs Total Concentration of Polymers at 40 ^{0}C

It is possible to obtain useful information about polymer-solvent interactions by analyzing the data which is obtained from viscosity measurement. Usually when two polymers are mixed together their blend becomes immiscible because thermodynamically the entropy of mixing is small for macromolecules. If specific interactions between components are strong, the polymer blends depend on concentration of polymer component ratio and temperature and become miscible.

When data given in Table 3.2, 3.3, and 3.4 are examined, it can be observed that the k_H values at all temperatures studied are around 0.2-0.3 for both pullulan and poly(ethylene glycol) indicating that water is a good solvent for both components. Pul/PEG blends with a composition of 80/20 and 50/50 have higher k_H values at all temperatures than pullulan or PEG alone in the solvent at the same temperature. On the other hand, the belnd with composition 20/80 has the same k_H value with PEG alone. These results show that there are attractive interactions between pullulan and PEG at 80/20 and 50/50 compositions, while at higher fractions of PEG the mixture does not exhibit any proof of favorable interactions in solution.

3.2 Miscibility of Pullulan/PEG Blends

3.2.1 Composition and Temperature Dependence of Miscibility Parameter

Based on the experimentally observed intrinsic viscosity [η] for ternary system, the miscibility criteria (ΔB $(dl/g)^2$, μ, α) were studied at 25, 30, 40 ^{0}C in a composition of (0.3, 0.2 and 0.1) with respect to pullulan. These parameters were calculated and tabulated in Tables 3.5, 6 and 7.

Table 3.5. Miscibility Parameter for Pul/PEG Blends at 25 ^{0}C

Blend	W_{pul}	ΔB $(dl/g)^2$	μ	α
Pul/PEG 80/20	0.3044	0.024	0.56	0.036
Pul/PEG 50/50	0.2032	0.0021	0.056	0.024
Pul/PEG 20/80	0.1041	-0.013	-0.32	-0.0072

Table 3.6. Miscibility Parameter for Pul/PEG Blends at 30 ^{0}C

Blend	W_{pul}	ΔB $(dl/g)^2$	μ	α
Pul/PEG 80/20	0.3025	0.025	0.66	0.032
Pul/PEG 50/50	0.2054	0.0021	0.051	0.019
Pul/PEG 20/80	0.1038	-0.011	-0.30	-0.0011

Table 3.7. Miscibility Parameter for Pul/PEG Blends at 40 ^{0}C

Blend	W_{pul}	ΔB $(dl/g)^2$	μ	α
Pul/PEG 80/20	0.3036	0.023	0.64	0.041
Pul/PEG 50/50	0.2044	0.0050	0.14	0.048
Pul/PEG 20/80	0.1053	-0.013	-0.36	-0.0031

Now we can observe related graphs which are plotted in Figure 3.5, 6, 7

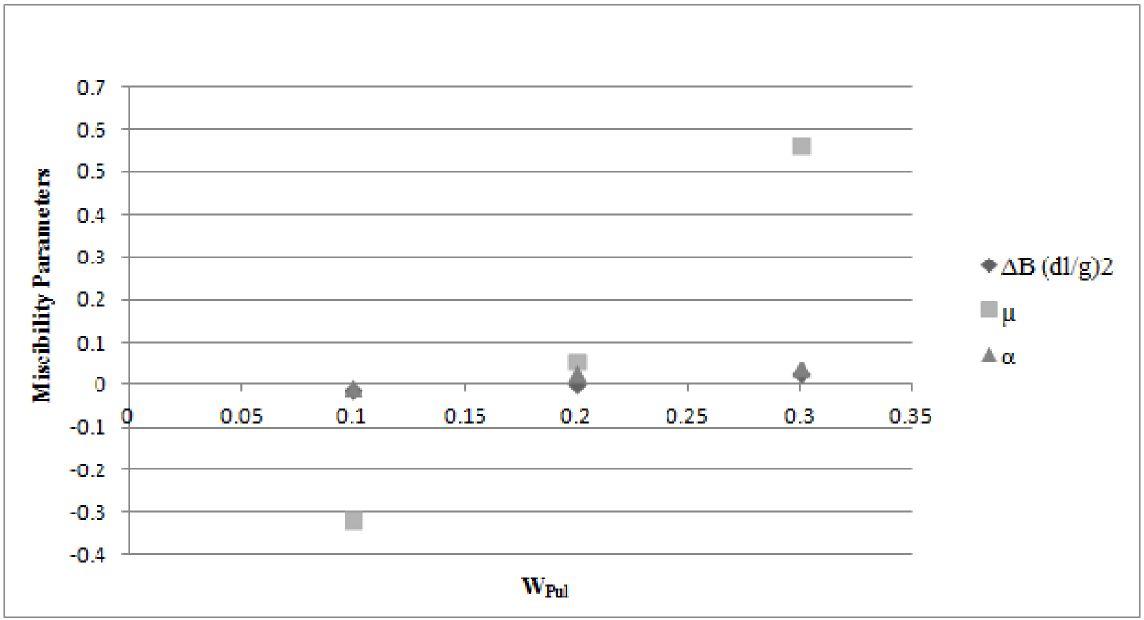


Figure 3.5. Miscibility Parameter (ΔB, μ, α) vs Weight Fraction of Pullulan at 25 ^{0}C

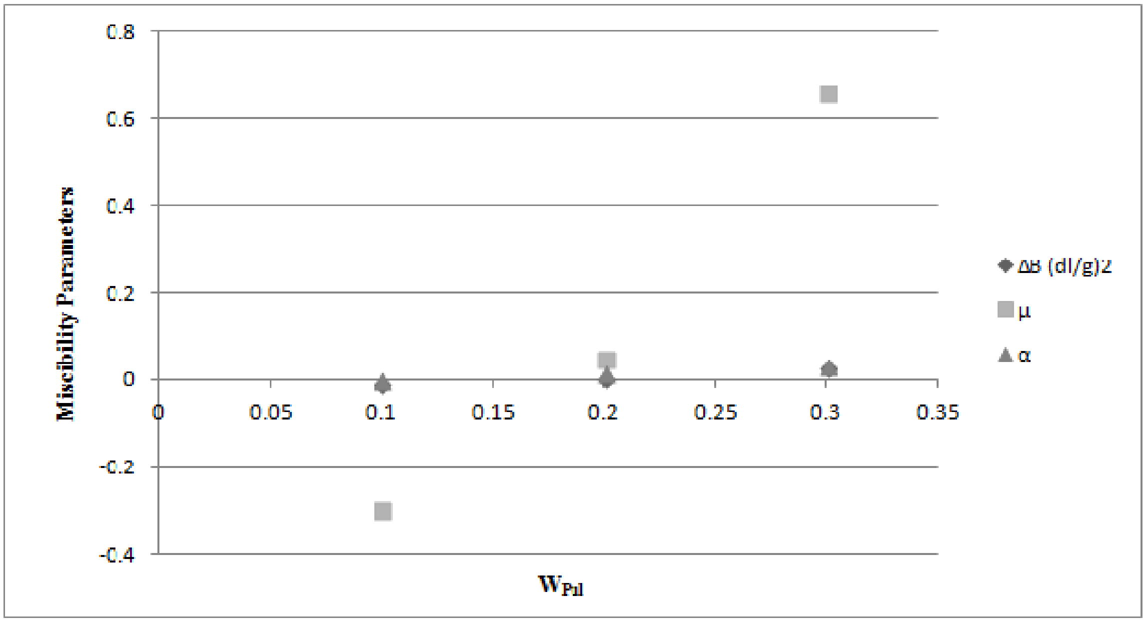


Figure 3.6. Miscibility Parameter (ΔB, μ, α) vs Weight Fraction of Pullulan at 30 ^{0}C

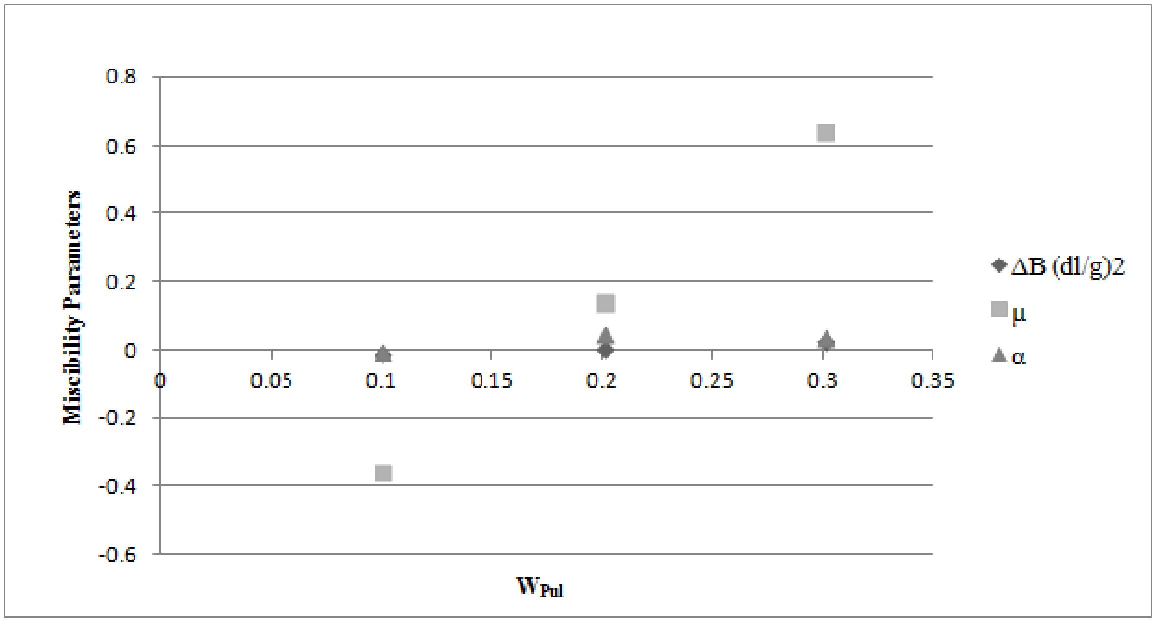
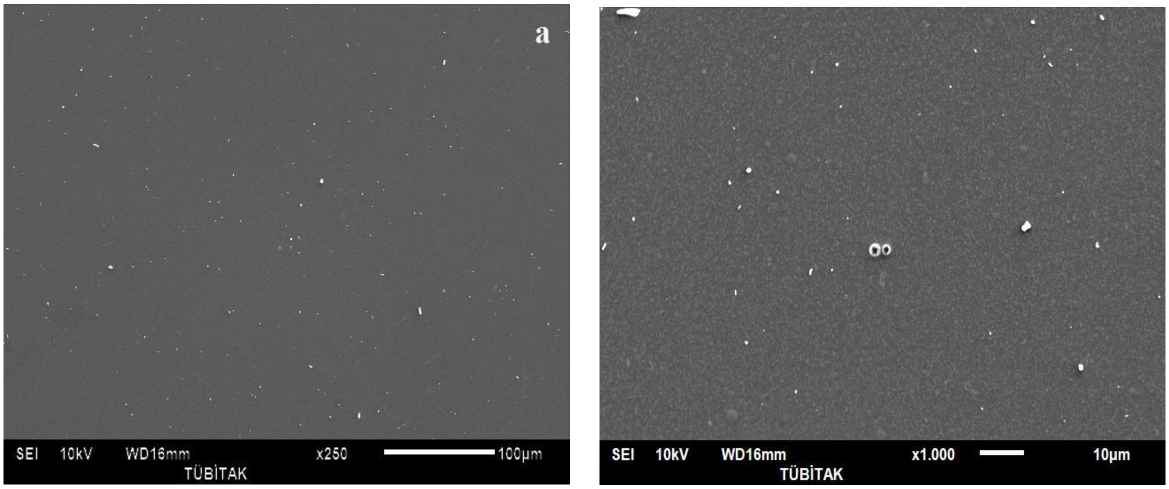


Figure 3.7. Miscibility Parameter (ΔB, µ, α) vs Weight Fraction of Pullulan at 40 ^{0}C

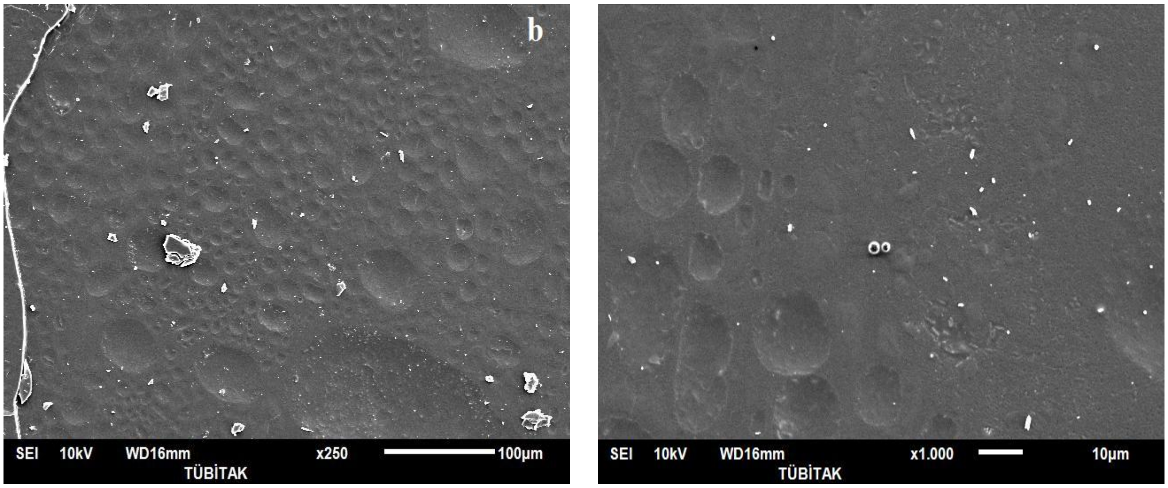
While Table 3.5, 6 and **7** studied based on Figures 3.5, 6 and 7, it can be observed that the miscibility parameters ΔB, α and µ reduce as the weight fraction of PEG (W_{PEG}) increases in polymer blends. Thus, the H-bonding interactions between pullulan and PEG overcome the intermolecular H-bonding among PEG chains at lower fractions of PEG. When the fraction of pullulan is higher in the mixture, pullulan chains may act as a pseudo solvent for shorter PEG chains since it is possible for pullulan chains to entangle around PEG chains and move together in solution. However, when PEG chains have a higher fraction in the blend than pullulan chains, this mechanism becomes less probable. Instead, pullulan and PEG chains act independently in solution. As a result, the sign of these parameters based on Chee and Sun et al. method indicates the miscibility of blends, so the positive values of ΔB, µ and α in blend composition (80/20 and 50/50) at all temperature show us the miscibility between two polymers. However pul/PEG (20/80) blend composition was found negative values which indicate phase separation in mixture at all temperatures. Therefore miscibility parameters show that, interactions between pullulan and PEG are favored at lower weight fraction of PEG. The results for all three blends are plotted in Figures 3.5, 6 and 7 at 25, 30 and 40 ^{0}C respectively. It can also be concluded that changing the temperature has no significant effect on miscibility between pullulan and PEG chains.

3.3 Morphology Study of Pullulan/Poly(ethylene glycol) Blends

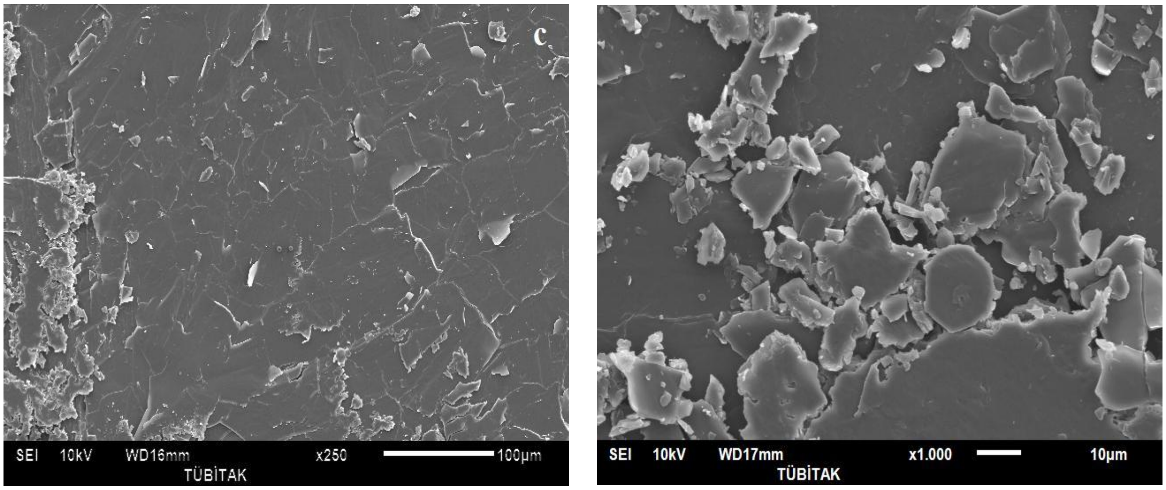
Solution-cast films of 100/0, 80/20, 50/50, 20/80 and 0/100 Pul/PEG were prepared to check the morphology of blends with scanning electron microscope (SEM). The results are given in figure 3.8.



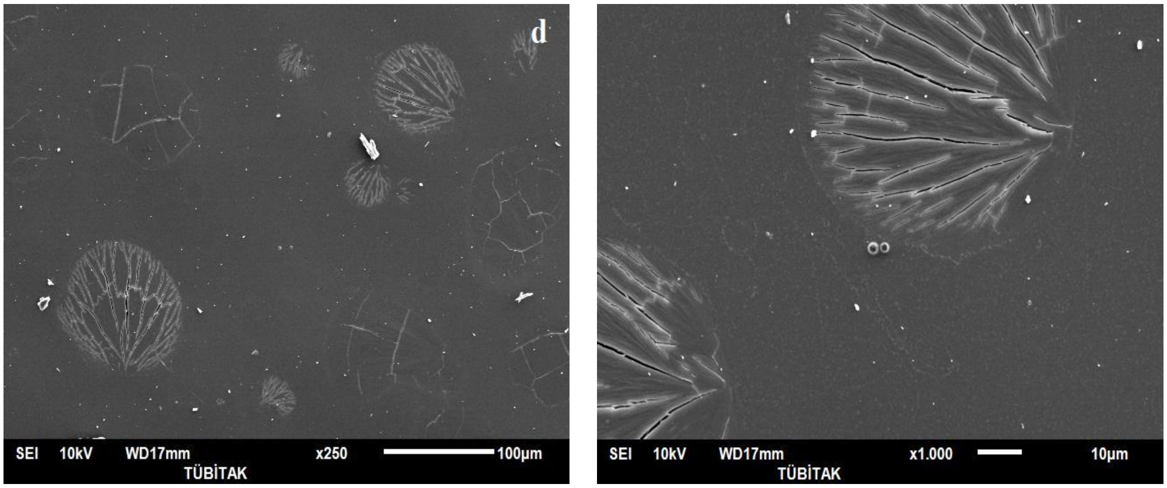
Scanning Electron Microscope for (a) Pure Pullulan Measured by High Magnification (X250 and X1.000)



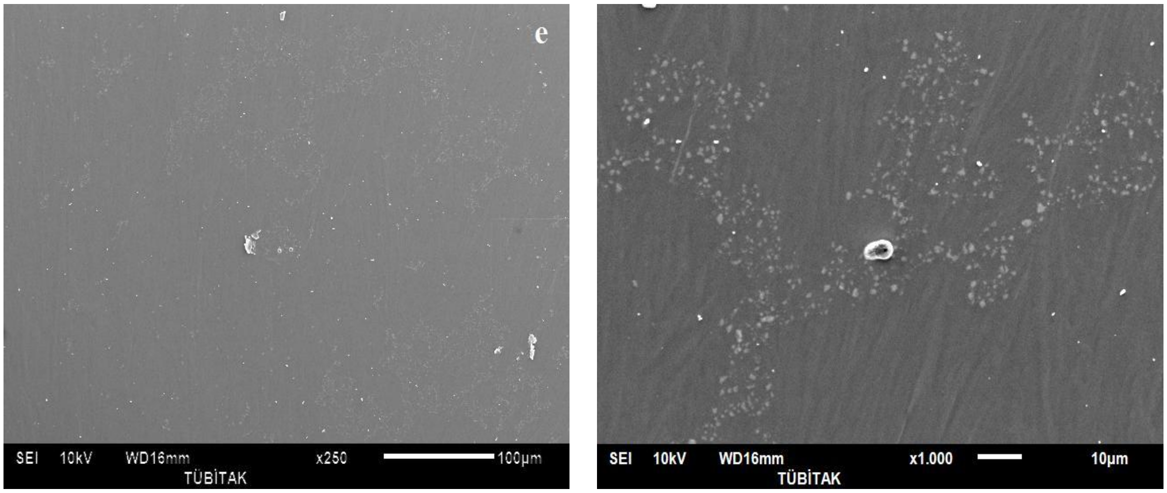
Scanning Electron Microscope for (b) Pul/PEG (80/20) Measured by High Magnification (X250 and X1.000)



Scanning Electron Microscope for (c) Pul/PEG (50/50) Measured by High Magnification (X250 and X1.000)



Scanning Electron Microscope for (d) Pul/PEG (20/80) Measured by High Magnification (X250 and X1.000)



Scanning Electron Microscope for (e) Pure PEG Measured by High Magnification (X250 and X1.000)

Figure 3.8. Scaning Electron Micrographs for (a) Pure Pullulan, (b) Pul/PEG (80/20), (c) Pul/PEG (50/50), (d) Pul/PEG (20/80) and (e) Pure PEG.

SEM pictures show that the surfaces of pure pullan and PEG films are totally homogenous. The Pul/PEG (80/20) composition blend shows homogeneity and it can be observed that PEG was well distributed in pululan matrix, whereas (20/80) blend indicated clear phase separation; it reveals that immiscibility. It can be concluded from the SEM pictures analysis that (50/50) blend is semi-miscible due to some phase separation observed. So it can be concluded that (80/20) composition blend has a good interaction between pullulan and PEG and the blend (20/80) is miscible whereas (80/20) blend composition is immiscible in the nature.

3.4 FTIR Analysis

This method provides useful information in reference to intermolecular interactions with vibrations of particular bands, and the positions of peaks that appear. Theoretically hydrogen bonding or other secondary interactions between chemical groups especially on the dissimilar polymers should indicate a shift in peak position of the participating groups. Moreover the shift in peak position will mainly depend on the strength of the interaction. The FTIR spectra of Pullulan, PEG and Pul/PEG blends (100/0, 80/20, 50/50, 20/80, 0/100) are shown in Figures. The FTIR spectra of pure pullulan, pure PEG and Pul/PEG (50/50) composition blend are compared to each other in Figure 3.13. The figure shows the FTIR spectra in the wave length range of 4000–500 cm^{-1}. Characteristic absorption bands which are observed in spectra can be summarized as follows;

The strong absorption at 3347.7 cm^{-1} indicates that pullulan had some repeating units of –OH and also the other strong absorption in 2925.2 cm^{-1} indicates C–H stretching of methylene. At wave number 1005.7 cm^{-1} appears strong absorption which is characteristic of a-D-glucopyranoside units.

On the other hand, in the PEG polymer spectrum appeared at 2890.2 cm^{-1} C–H stretching of methylene groups, at 1466.4, 1363.3 cm^{-1} C–H bonding is assigned to stretching vibration and 1153.9, 1102.3 and 1057.2 cm^{-1} are C–O banding which are shown.

The spectrum of the blend (50/50) composition C–H stretching at 2890.2 cm^{-1} has a small shift to 2887 cm^{-1}and the other C–H stretching vibration and symmetric indicated lower trend of interaction between pullulan and PEG. This wave numbers described as tend towards immiscibility of (50/50) composition of polymer blend.

Figure 3.11 was recorded the spectrum of (80/20) composition which indicated strong –OH bonding appears at 3273.87 cm^{-1} and C–H stretching at 2885.69 cm^{-1}, the hydroxyl characteristic bands shifted towards lower wave numbers. This wavelength strongly supports the existence of intermolecular hydrogen bonding between the hydroxyl groups of pullulan and PEG. It is noticed that the hydroxyl stretching bands became much broader with increasing pullulan content.

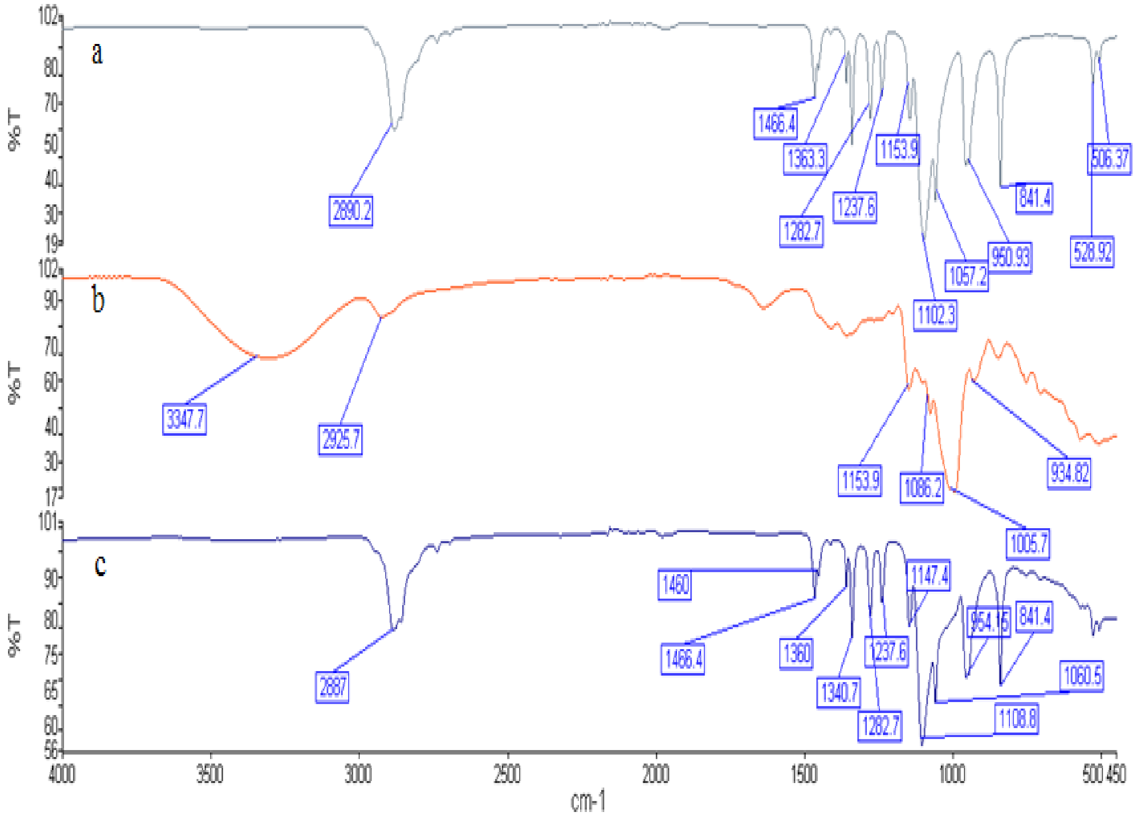


Figure 3.9. FTIR Spectra of (a) PEG, (b) Pulluan and (c) Pul/PEG (50/50)

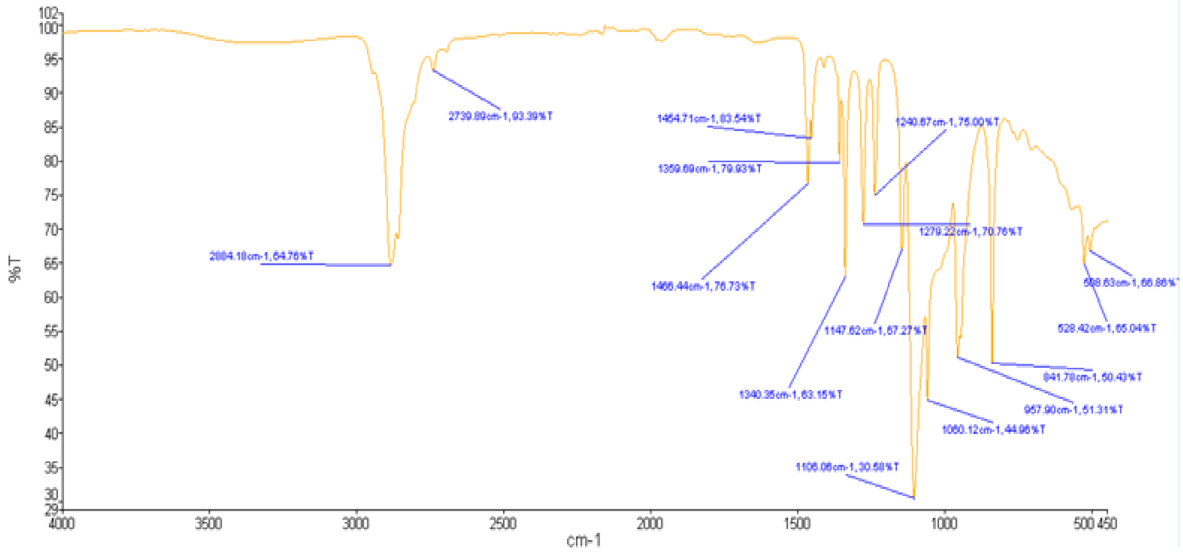


Figure 3.10. FTIR Spectra of Pul/PEG (20/80)

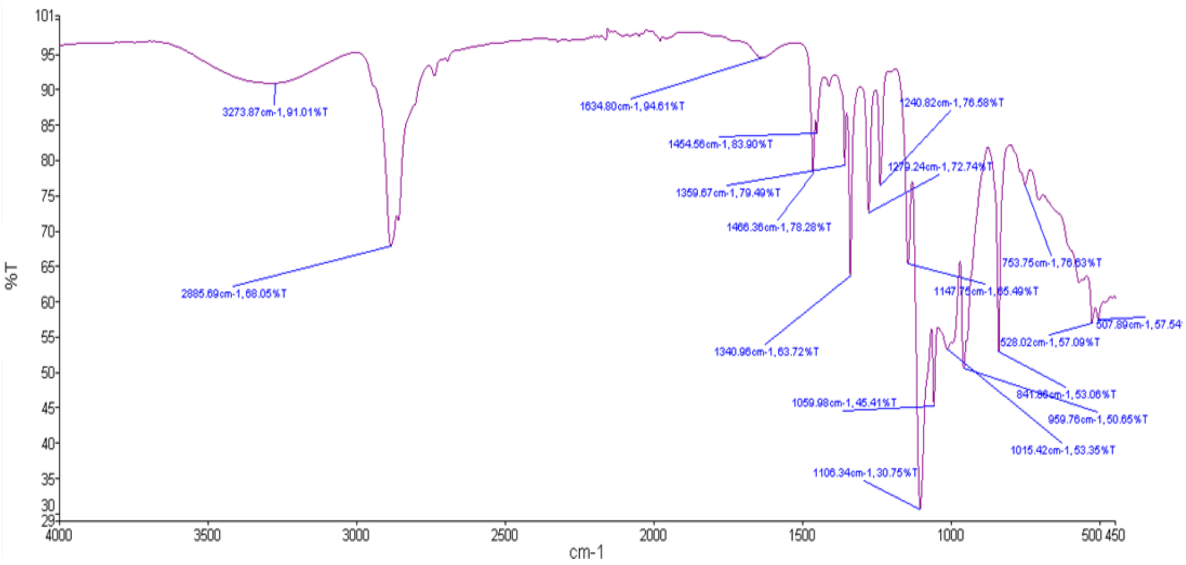


Figure 3.11. FTIR Spectra of Pul/PEG (80/20)

H-bonding interacts between pullulan and PEG chain backbone in polymer blend.

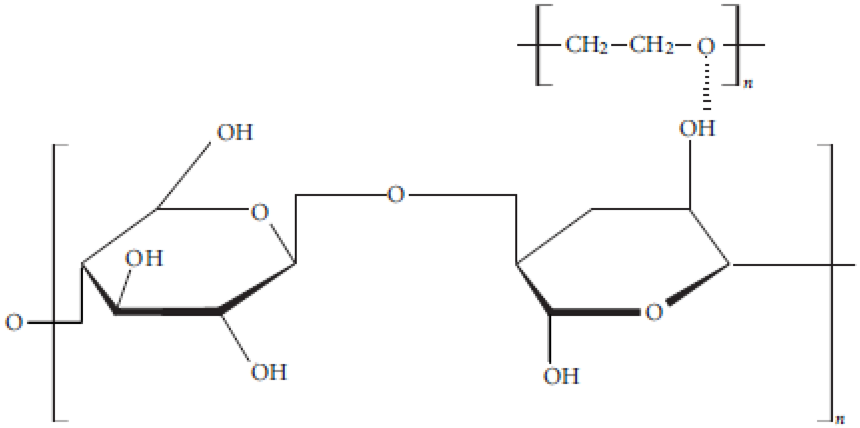


Figure 3.12. Schematic of H-bonding Between Hydroxyl Group of PEG and Pullulan

3.5 DSC Analysis

The thermal properties of pullulan, PEG and their blends films were studied by means of DSC analysis. The melting point of the polymer films were recorded in the range of 30-120 °C for as shown in figures.

Differential scanning calorimetry can be used for examining polymeric films to determine thermal transitions. This transition from solid to liquid state will require heat flowing. Into the system, heating of the samples show endothermic phase transition. The melting process exhibit endothermic positive peak in the DSC curve this measurement provides valuable information about miscibility for various polymer blends composition. Thin films of individual polymers pullulan, PEG, 80/20, 50/50 and 20/80 composition were shifted means DSC- T_m. As it observed the films were studied in the range of 30-120 °C at a heating rate at 10 ^{0}C as shown in figures. The melting point was taken as the mid-point of the melting peak in the DSC curves. In pure pullulan curves, we can see a small peak around 70°C in the first heating curve, and in pure PEG sharp peak in 67.03 °C. Thermo gram of 80/20 Pul/PEG blend showed peak at T_m = 64.64 °C and these measurement shifted to higher amount T_m = 66.31 °C in 20/80 Pul/PEG. As a result, the blend curves reveal that the melting temperature of peaks reduced with increasing weight fraction of pullulan which confirmed intermolecular interaction between pullulan and PEG 80/20 composition.

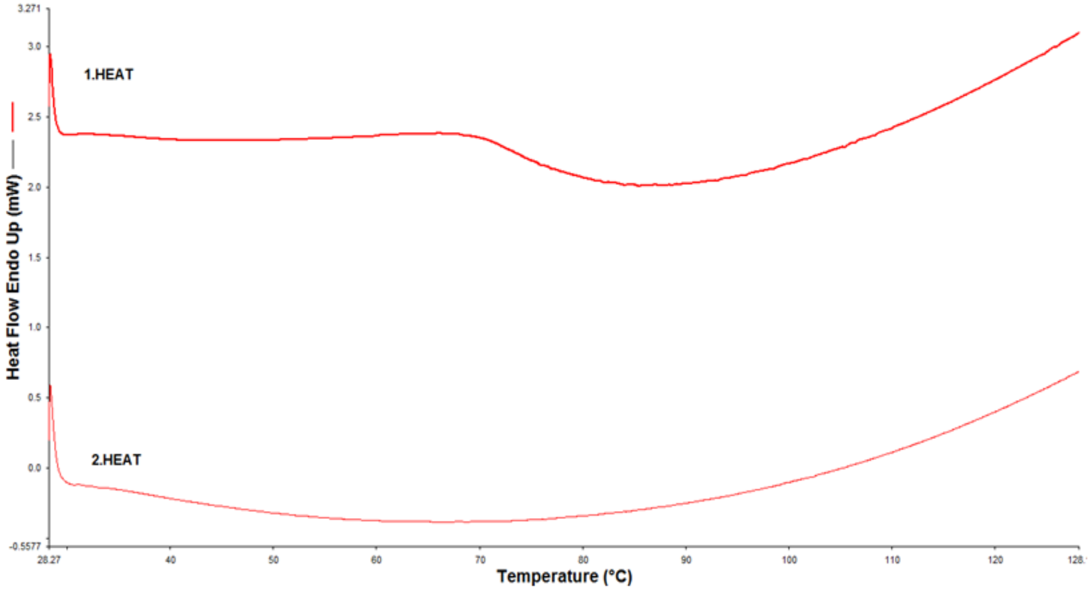


Figure 3.13. (a) DSC trace of Pure Pullulan

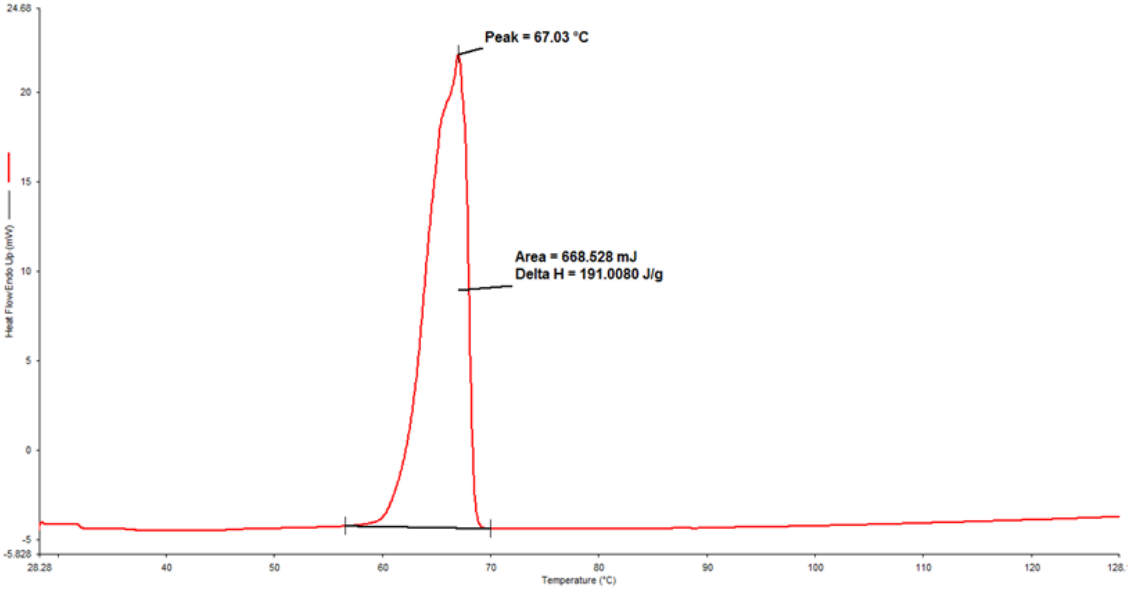


Figure 3.14. (b) DSC trace of Pure PEG

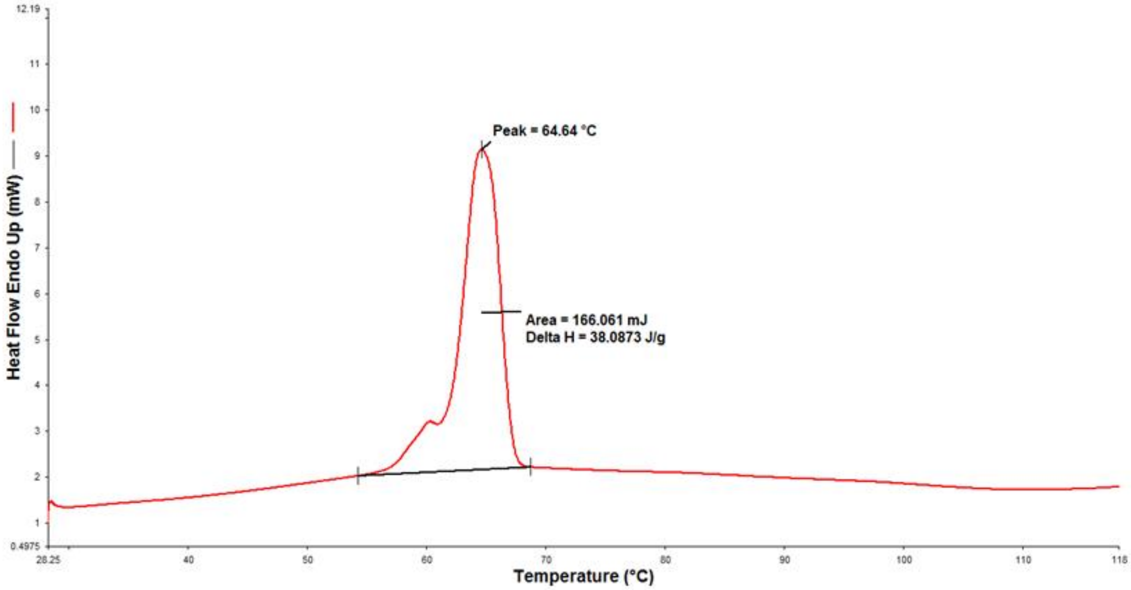


Figure 3.15. (c) DSC trace of Pul/PEG (80/20)

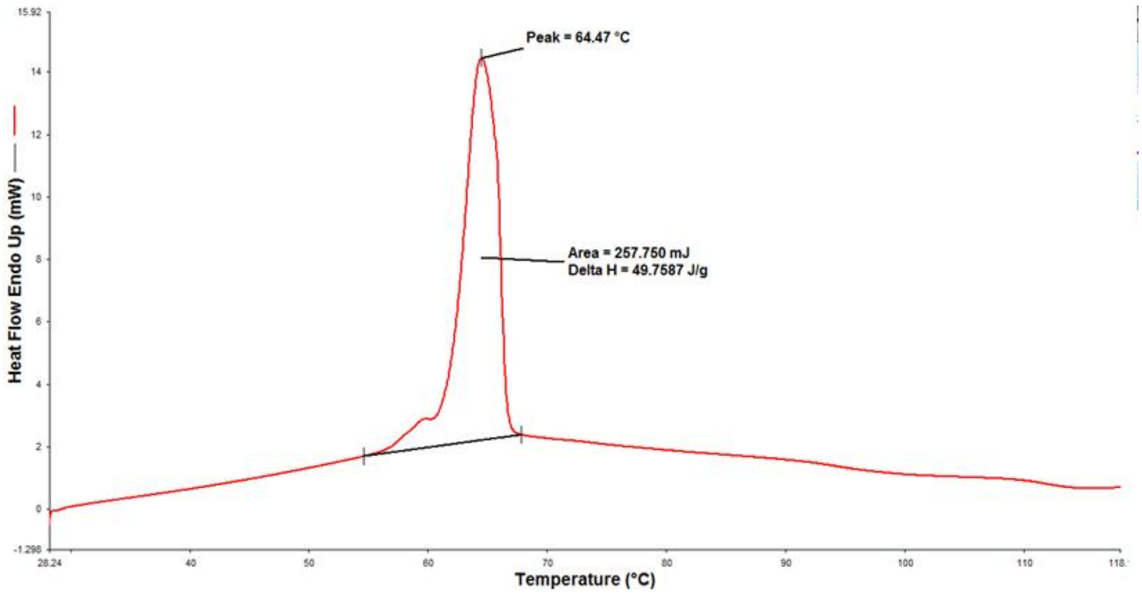


Figure 3.16. (d) DSC trace of Pul/PEG (50/50)

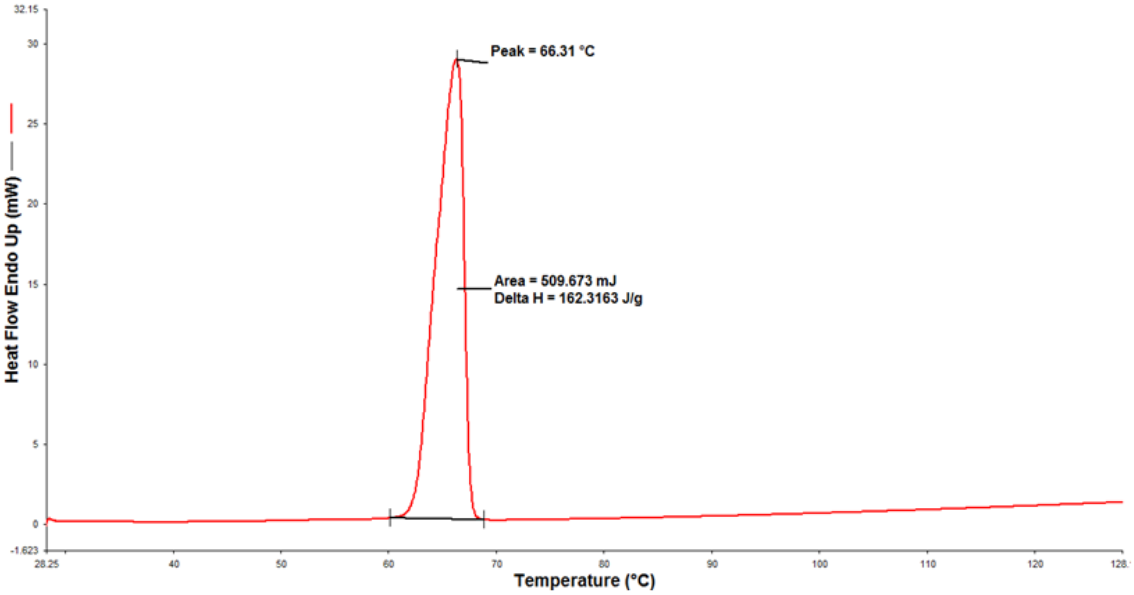


Figure 3.17. (e) DSC trace of Pul/PEG (20/80)

Chapter 4

CONCLUSIONS

The miscibility of Pul/PEG blends in water has been investigated by dilute solution viscometry and other techniques such as FTIR, SEM and DSC in the solid state. The values of miscibility parameters revealed compatibility of the system with increasing pullulan fraction. Pul/PEG blend with 80/20 and 50/50 composition are miscible in solution according to positive miscibility parameter values obtained. On the other hand, Pul/PEG (20/80) sample is immiscible according to negative values of ΔB, μ and α. It is also observed that temperature has no significant effect on the miscibility of Pul/PEG system within the temperature range studied.

Furthermore, morphology studies also reveales homogeneity in dispersion when pullulan content is more than 50% in the blend. FTIR analysis shows that there are specific intermolecular interactions of H-bonding between pullulan and PEG at higher pullulan content. SEM and DSC analysis also confirms hydrogen bonding between polymer blend 80/20 compositions as well. Both solution studies and investigations in the solid state indicate miscibility between pullulan and PEG with increasing pullulan fraction. The sample with 80/20 Pul/PEG fraction is miscible while 50/50 Pul/PEG sample is semi-miscibile and 20/80 Pul/PEG sample is immiscible.

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