Miscibility studies of Polyethylene Glycol with Polystyrene in Toluene by Various Physical and Advanced Techniques

R Padmanaban, K Venkatramanan

Department of Physics, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya, Enathur, Kanchipuram – 631561, Tamilnadu, India

E-mail: kv.scsvmv@gmail.com

Abstract. Polyethylene glycol (PEG) is a chemical that has an extensive variety of applications in the world of medicine. It is used as a base to manufacture certain medicines, assist in drug delivery, and is also used as an agent in some medical procedures. It is an osmotic laxative. Polyethylene glycol works by retaining water in the stool, resulting in softer stools and more frequent bowel movements. Polyethylene glycol does not affect glucose and electrolytes in the body. PEG refers to a hydrocarbon molecule that can have a variable size, and different sizes can have different physical properties, giving this compound a great deal of flexibility in its application. In the present study, Polyethylene Glycol (PEG) (Molar mass : 1500) is blended with Polystyrene (PS) (Molar mass: 35000) in Toluene. The miscibility nature of the poly blend is analyzed by Ultrasonic velocity, viscosity, density and refractive index techniques at 303K. The compatibility nature of the blend is confirmed by Differential Scanning Calorimetry (DSC) studies.

1. Introduction

Polyethylene Glycols (PEG) have extensive applications in pharmaceutical preparations, cosmetics and in the metal costing process [1]. Polyethylene glycol is edible polymer film used for food packing and directly in foodstuffs [2]. To satisfy the growing needs of new materials with specific properties such as engineering materials, new polymers have been synthesized [3]. However, the mixture of two or more polymers, forming a polymer blend, continues to be an economical method to obtain new polymeric materials [4]. Blending of polymers is one of the simplest methods to obtain a variety of physical and chemical properties from the constituent polymers at a molecular level. The gain in newer properties depends on the degree of compatibility or miscibility of the polymers. There are a number of techniques to study the miscibility of polymer blends such as ultrasonic, viscosity, refractive Index, FTIR, XRD, DSC and SEM [5]. The final properties of a polymeric blend will commonly depend on the properties of its polymeric components, its composition and mainly on the miscibility of the constituent polymers. Several researchers [6-9] have reported on the miscibility studies of PEG. In the present case, PEG (1500) and PS (35000) polymer blend solutions are prepared in toluene and their miscibility nature is analysed using density, viscosity, ultrasonic velocity, and refractive index measurements. By solution casting method, polymer blend films are prepared and their miscibility nature is further analysed using DSC techniques. The compatibility of these polymer blends is discussed and it is concluded that the presence of hydrogen bonding groups in these two polymers is responsible for the polymer-polymer interaction.

2. Material and Methods

In the present study, Polyethylene Glycol (PEG 1500) is blended with Polystyrene (PS 350000) in toluene. High purity spectra grade PEG 1500 and PS 35000 are obtained from KAVIN SCIENTIFIC, Chennai, India. 1% concentration of PEG 1500 and PS 35000 are separately prepared by dissolving 4 gms of each polymer in 400 ml Toluene. Then various compositions of the blend PEG 1000 / PS 35000 in the following ratio (0/100, 20/80, 40/60, 50/50, 60/40, 80/20, 100/0) are prepared by proper mixing at 30º C (accuracy ± 0.5 º C). Magnetic stirrer [REMI make] is used for this purpose at a rate of 1000 rpm. The relative viscosity of the polymer solutions is studied for all the blend composition ranges at 303K using Brookfield Viscometer (USA) (accuracy ±0.01cP). The temperature is maintained using a thermostat with a thermal stability of ± 0.05 K. The density values are measured using specific gravity method. The mass of the liquid is measured using a K-ROY make electronic balance, with an accuracy of ±0.001gm. Refractive index studies are performed at 303 K using Abbe Refractometer (uncertainty ± 0.5%). The ultrasonic velocity measurements are performed using Mittal make single frequency Ultrasonic interferometer at 2 MHz (F-81 model) (uncertainty ± 0.01m/s). The temperature is maintained at 303 K by circulating water from a thermostat with a thermal stability of ± 0.05 K through the double wall jacket of the cell. The glass transition temperature is studied using Differential Scanning Calorimetry (DSC), NETZSCH Technologies, Chennai.

3. Results and Discussion

Viscometry is a simple and effective technique for monitoring the interactions of polymer blend solutions. From these measurements, relative viscosity of pure polymers and their blends are obtained. Figure 1 shows the variation of PEG 1500 / PS 35000 in toluene at 313 K for different weight fractions of polymer 1 and polymer 2 respectively. From this figure, the variation is linear from 50/50 to 100/0 blend compositions and non linear for remaining blend composition ranges. From this, it may be concluded that the blend system is partially miscible for blend composition ranges from 50/50 to 100/0.

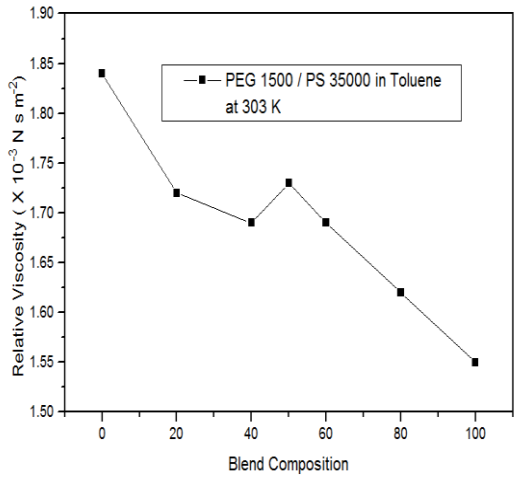

Figure 1. Variation of Relative viscosity against blend composition of PEG 1500

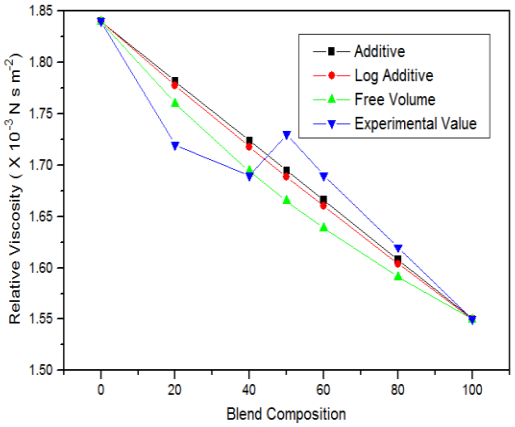

Figure 2. Variation of Relative viscosity against blend composition of PEG 1500 by additive rule

Gupta et al [10] have recommended viscometric method to study polymer-polymer miscibility. The basic idea of using viscosity as a parameter for compatibility determination of polymer blends lies in the fact that in solution the repulsive interaction may cause shrinkage of polymer coils resulting in the viscosity of the polymer mixture that is lower than the value calculated from viscosities of the pure components on the assumption of additive law. Venkatramanan et al [7] have used a few empirical and semi empirical equations for predicting the miscibility of polymer blends based on viscosity viz., the additive rule, log additive rule, and free volume additive rule given by Eq. 1, Eq. 2 and Eq. 3.

$$\eta_b = W_1\eta_1 + W_2\eta_2 \quad (1)$$

$$\log \eta_b = W_1 \log \eta_1 + W_2 \log \eta_2 \quad (2)$$

$$1/\log \eta_b = W_1(1/log\eta_1) + W_2(1/log\eta_2) \quad (3)$$

Where η_b is the viscosity of the blend, η_1, η_2 that of the components and W_1, W_2 the weight fractions of the components.

In the case of completely miscible blends, that is 100% miscible blends, the experimental values will be the same as the values calculated from the additive rule of the mixture. When the blend is less than 100% miscible or partially miscible the values predicted from log additive rule of the mixture will be close to the experimental value. Figure 2 shows the variation of relative viscosity against blend composition of PEG 1500 using additive rule method. Here from 50/50 to 100/0 blend composition range, it is observed that the experimental values are positively deviating. This shows that the blend is miscible. For other blend compositions, the experimental values are negatively deviating which means that the blend may be immiscible. From this, it is concluded that the blend system is partially miscible from 50/50 to 100/0 blend compositions. For further confirmation density studies are performed. It is observed from the density results (Figure 3) that in the composition range from 50/50 to 100/0, the variation is linear showing the miscible nature of the blend and from 0/100 to 50/50 composition, the blend is immiscible due to non-linear variation. Throughout the system, the blend is semi-compatible. To confirm the compatibility nature of the blend further, refractive index studies are carried out. Refractive index is a useful technique to analyze miscibility of polymer blends. In the present case (Figure 4), for the composition range from 0/100 to 50/50, the variation is nonlinear which shows that the blend is immiscible and for other composition ranges, the variation is linear which shows the miscible nature of blends. From this, it may be concluded that the blend system is partially miscible from 50/50 to 100/0 composition range. For further confirmation, ultrasonic velocity was calculated.

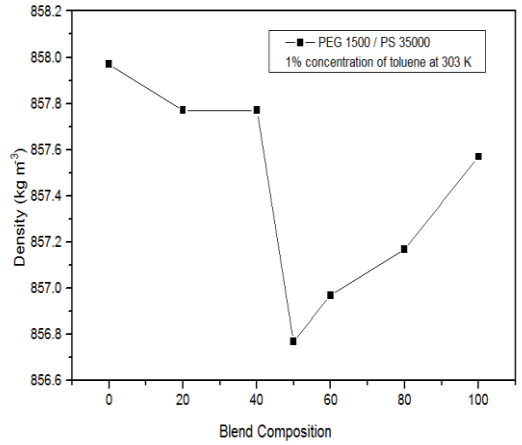

Figure 3. Variation of Density against blend composition of PEG 1500

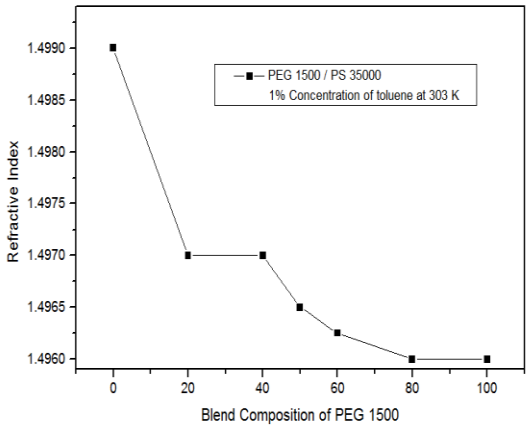

Figure 4. Variation of Refractive Index against blend composition of PEG 1500

Ultrasonic technique plays a vital role in determining the compatibility of the polymer blends. It has been reported by Sidkey et al [11] that (a) if the variation of ultrasonic velocity with blend composition is of S -type, the blend is immiscible, (b) if the ultrasound velocity shows a linear relation with blend composition, then the blend is compatible or miscible and (c) for semi compatible system, the nature of the curve is in between straight line and s- shape. In the present case [PEG 1500 / PS

35000] the nature of the curve is s- shape (Figure 5). It may be concluded that the blend is immiscible in nature. To confirm further, DSC studies were done.

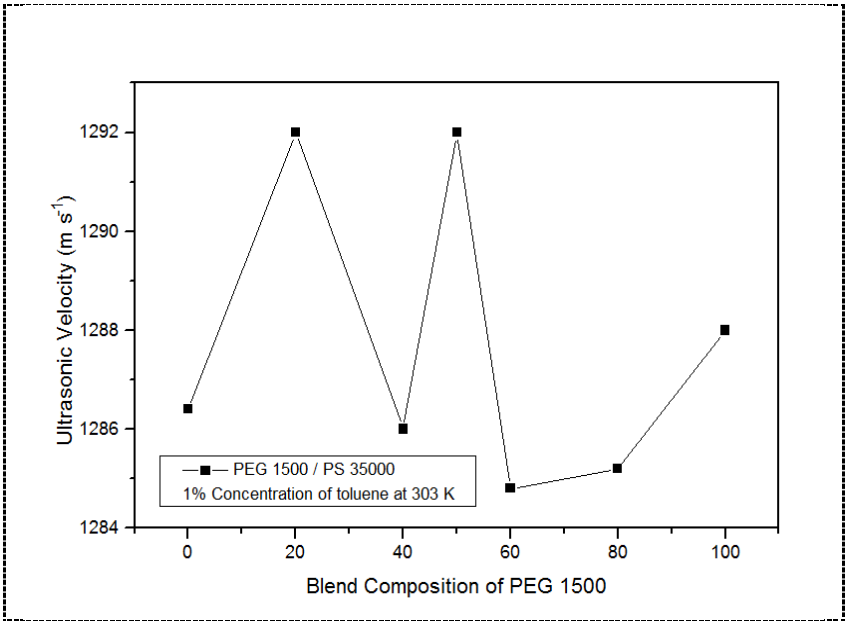

Figure 5. Variation of Ultrasonic Velocity against Blend Composition of PEG 1500

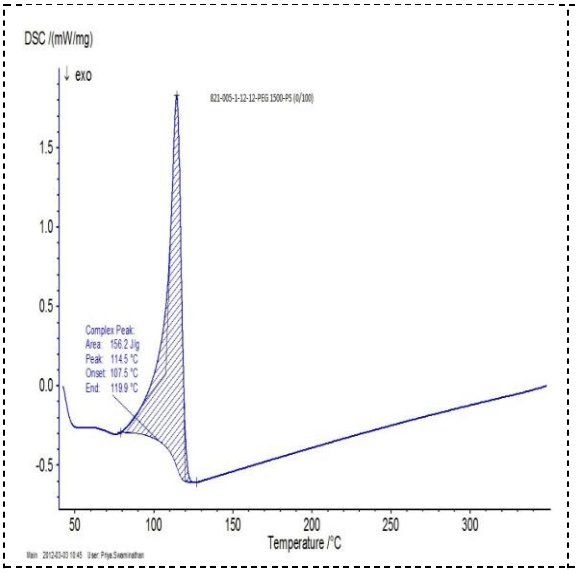

Figure 6. DSC Studies of PEG 1500 / PS 35000 in Toluene at 303 K (0/100 composition)

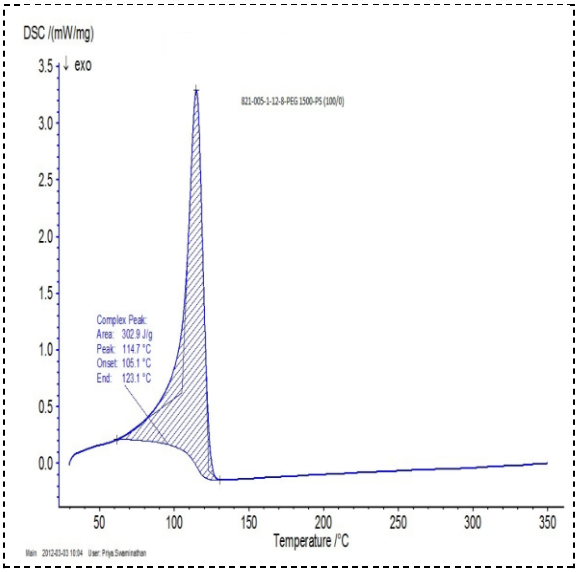

Figure 7. DSC Studies of PEG 1500 / PS 35000 in Toluene at 303 K (100/0 composition)

DSC is a valuable thermal analysis technique which provides with important information on the glass transition of polymer blends. The miscibility and interaction between components are the most important aspects for defining polymer blends. Measuring the glass transition temperature of the desired polymer blend will quickly and easily determine their compatibility. The blend system PEG 1500 / PS 35000 was first cooled from 120°C to -140°C at 5K/min and then measured by heating from -160°C to 600°C at 10 K/min in nitrogen atmosphere at 50ml/min to determine the temperature at which the glass transition occurs. The glass transition range for PS 35000 extends over an area of 156.2 J/g between 107.5°C and 119.9°C with a peak at 114.5°C. For PEG 1500, it extends over an area of 302.9 J/g between 105.1°C and 123.1°C with a peak at 114.7°C. Figure 8 shows the glass transition range which extends over an area of 260.4 J/g for PEG 1500/PS 35000 blend system [50/50] between 111.1°C and 124.2°C has a peak at 118.5°C. The occurrence of just one glass transition observed in the polymer blend system PEG 1500 / PS 35000 (50/50 blend composition) confirms that polymer components are compatible [12-14] from 50/50 to 100/0 blend compositions.

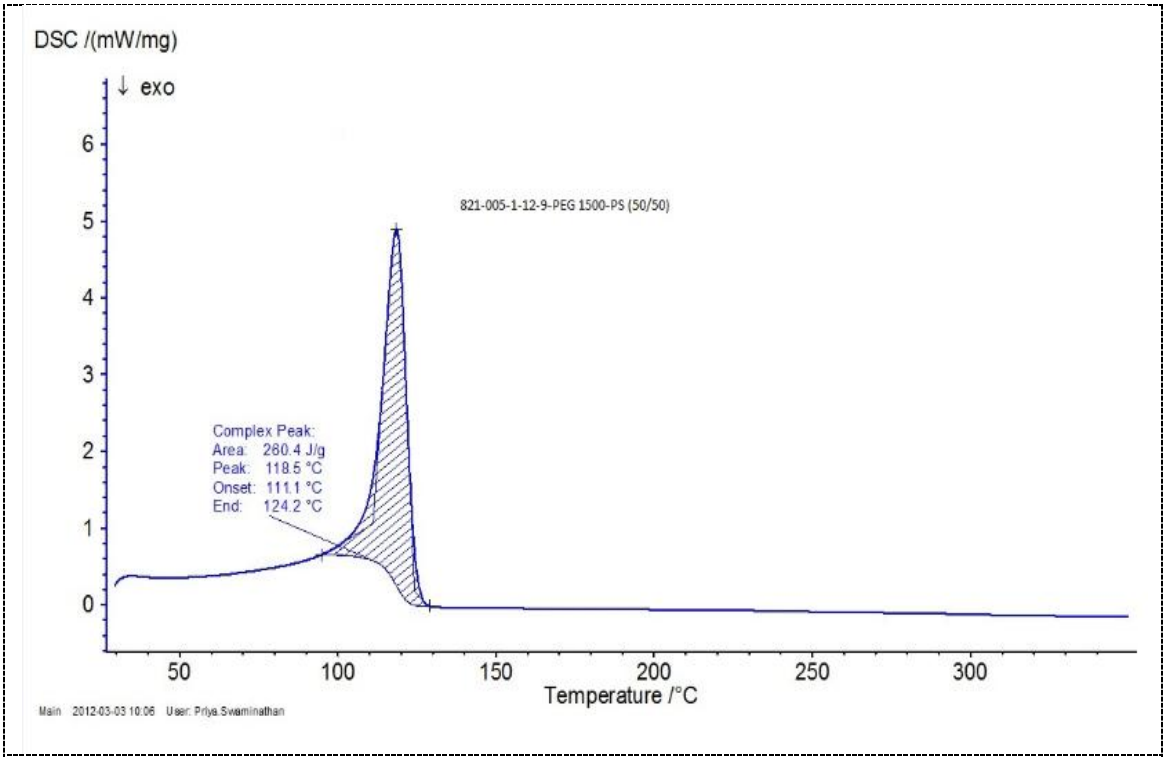

Figure 8. DSC Studies of PEG 1500 / PS 35000 in Toluene at 303 K (50/50 composition)

4. Conclusion

PEG 1500 is blended with PS 35000 in toluene at 303 K and the compatibility nature of the blend is analysed using various physical methods like viscosity, density, refractive index and ultrasonic and DSC techniques. The blend system showed partial miscibility from 50/50 to 100/0 blend compositions. DSC studies confirmed the partial miscibility nature of this blend.

References

[1] Syal V K, Anita Chauhan, and Suvarcha Chauhan 2005 *J. Pure Appl. Ultrason.* **27** 61-69
[2] Sudhir Ramswamy Illiger, Chandralekha Fadnis, Demappa T, Jayaraju J and Keshavayya J 2009 *Carbohydr. Polym.* **75** 484-488
[3] Chowdoji Rao K, Subha M C S, Suresh Reddy C, Kumara Babu P, Sudhaka K, Prabhakar M N, Maruthi Y, and Sajan Kumarji Rao 2013 *Int. J. Basic App. Chem. Sci.* **3** 73-83
[4] Crispim E G, Rubira A F and Muniz E C 1999 *Polym. J.* **40** 5129-35

[5] Sudharsan Reddy K, Prabhakar M N, Kumara Babu P, Venkatesulu G, Sajan Kumarji Rao U, Chowdoji Rao K and Subha M C S 2012 *Int. J. Carbohydr. Chem.* **2012** 1-9
[6] Mruthyunjaya Swamy T M and Siddaramaiah 2007 *J. Appl. Polym. Sci.* **104** 2048-53
[7] Venkatramanan K, Padmanaban R and Kalidass D 2013 *J. Pure Appl. Ultrason*. **35** 105-108
[8] Venkatramanan K and Arumugam V 2008 *AIP Conf. Proc*. **1004** 235-40
[9] Jayaraju J, Basavaraju K C, Keshavayya J and Rai S K 2006 *J. Macromol. Sci., Phys.* **45** 741-51
[10] Ashok Kumar Gupta and Gautam Kumar Sah 2013 *Nanosystems: Physics, Chemistry, Mathematics* **4** 670–79
[11] Sidkey M A, Yehia A A, Abd El Malaka N A, and Gaafar M S 2002*, Mat. Chem. Phys*. **74** 23-32
[12] Vasile Cristian Grigoras and Virgil Barboiu 2008 *Reveu Roumaine de Chimie* **53** 127-31
[13] Marina Vivas de Meftahi, Jean MJ Frechet 1988 *Polymer* **29** 477-82
[14] Everaert, Groeninckx, Koch and Reynaers H 2003 *Polymer* **44** 3491–08