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Thermoacoustical Studies of Polyblend Solutions

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Abstract: ***The ultrasonic veocity and their related thermoacoustical parameters were successfully employed to understand the miscibility and molecular interactions in polymer blends. In present investigation ultrasonic velocity, density measurements have been performed on solution blends of polybutadiene (PB) – polystyrene (PS) in various blend ratios using THF as solvent. These measurements have been observed to deviate from linearity with variations in blend ratio. Ultrasonic velocity and density measurements are done at 2MHz frequency and at temperatures 293K, 298K, 303K, 308K and 313K.***

Keywords: ultrasonic velocity, polybutadiene, polystyrene, blend

1. Introduction

Blending of polymers is one of the simplest means to obtain variety of physical and chemical properties from the constituents polymers[1]. The gain in the newer properties depends on degree of compatibility or miscibility of polymers at molecular level. Generally polymer-polymer miscibility is due to some specific interactions like dipole-dipole forces, hydrogen bonding and charged transfer complexes between polymer segments. A literature survey reveals various techniques of studying the miscibility of polymer blends [2]. Singh et al,[3,4] have suggested the use of ultrasonic velocity and viscosity measurements for investigating the polymer compatibility. Sidkey M.A. et al[5] has studied ultrasonic investigations of some rubber blends. Singh and Singh[6] have measured ultrasonic velocity and absolute viscosity in solution of compatible, incompatible and semicompatible blends. In present investigation polybutadiene rubber, Polystyrene are materials used, because these materials are recognized as high performance polymers. The present paper discusses in detail extensive investigations of ultrasonic velocity, density, adiabatic compressibility, intermolecular free length, acoustical impedance and relaxation time measurements of PB+PS blends in various blend ratios.

2. Materials and Methods

2.1 Materials and preparation of solutions blends . Master solutions of Polybutadiene rubber and Polystyrene have been prepared by dissolving these materials separately in desired concentrations (1gm in 100ml) in THF at room temperature(30^0C) and then kept for 4 hours in air tight bottles, resulting in transparent solutions. After this solution blends have been prepared in various blend ratios of PBR/PS (100/0, 80/20, 60/40, 40/60, 20/80, 0/100) taking appropriate amount from the stock solution for ultrasonic velocity, density measurement.

2.2 Ultrasonic Velocity measurement is done by MHF-400 high frequency pulser receiver (supplied by Roop Telsonic ultrasonix Ltd.) Ultrasonic pulser receiver is advanced technique which provides unique low cost ultrasonic measurement capability. The instrument has been spike pulser and broadband receiver. The receiver has max gain of 103dB, adjustable in minimum step of 1dB. 4 high pass and low pass filters each facilitate frequency cut off for optimization of received signal.

Pulser section of instrument generates electronic pulses of controlled energy which are converted into short ultrasonic pulses when applied to an ultrasonic transducer. In receiver section voltage signals produced by the transducer which represent the received ultrasonic pulses are amplified. The amplified radio frequency (RF) signal is available as an output for display. The ultrasonic velocity is calculated from the captured signals automatically and is displayed on the screen.

The ultrasonic velocity measurement is done at 2MHz frequency and at temperatures 293^0K, 298^0K, 303^0K, 308^0K, 313^0K for PBR/PS solutions blends in different ratios. The densities of all solution blends have been measured by pycnometer at temperatures 293^0K, 298^0K, 303^0K, 308^0K, 313^0K.

Ultrasonic velocity, density measurements change even with very small change of temperature. Therefore for such measurements it is very necessary to keep temperature constant accurately. Plasto craft thermostate (LTB -10) maintains desired accurate constant temperature with accuracy of $\pm 0.1^0$C in temperature range -10^0C to 95^0C.

3. Theoretical Formulations

1. Ultrasonic velocity is given by

$$u = \frac{2d}{t} \text{ m/sec}$$

Where, d – separation between transducer & reflector

t- travelling time period of ultrasonic wave

2. Density is given by

$$\rho = \left(\frac{M_1}{M_w}\right)\rho_w \quad \ldots.\text{Kg/m}^3$$

Where, M_l and M_w are the mass of liquid and water respectively.

ρ_w - density of water

3. Adiabatic Compressibility is given by

$\beta_a = \frac{1}{u^2\rho}$ …m^2/Newton

Where u is the velocity of sound in liquid and ρ is the density of the liquid for particular concentration of the constituents.

4. Intermolecular Free Length is given by

$L_f = K_j(\beta_a)^{1/2}$

Where K_j- Jacobson's constant & β_a- Adiabatic compressibility

5. Relaxation Time is given by

$\tau = \frac{4}{3}\eta\beta_a$ …… sec

Where β_a- Adiabatic compressibility and η- Viscosity

6. Acoustical Impedance

$Z = \rho u$ Kg/m^2 sec

Where Z- acoustical impedance, ρ- density and u- ultrasonic velocity

4. Results and Discussion

Fig1 shows that ultrasonic velocity decreases with increase in temperature at 2MHz frequency. The phase equilibrium of polymer solutions has strongly affected by change in solution temperature. The rise or fall of ultrasonic velocity for various blend ratios is due to polymer solvent interactions and solid content of each polymer. Non linearity in ultrasonic velocity suggests immiscibility of polymer blends. Increase in Ultrasonic

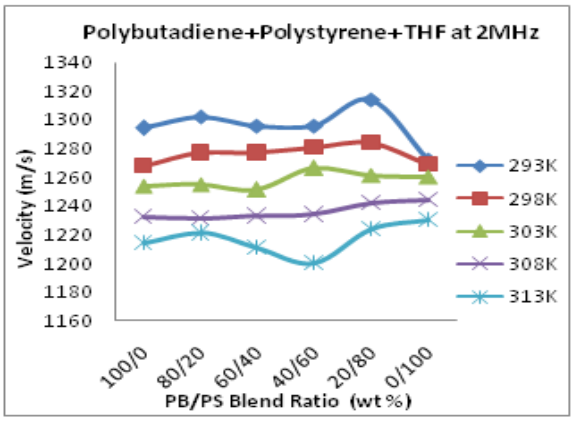

Fig1 velocity for blend ratio 20/80 indicates that there are strong molecular interactions and closed packed structure of component molecules.

Fig2 shows that density varies non-linearly for solution blends at various temperatures. The significant increase in density for blend ratio (20/80) shows polymer-polymer relative polarity and strong molecular interactions.

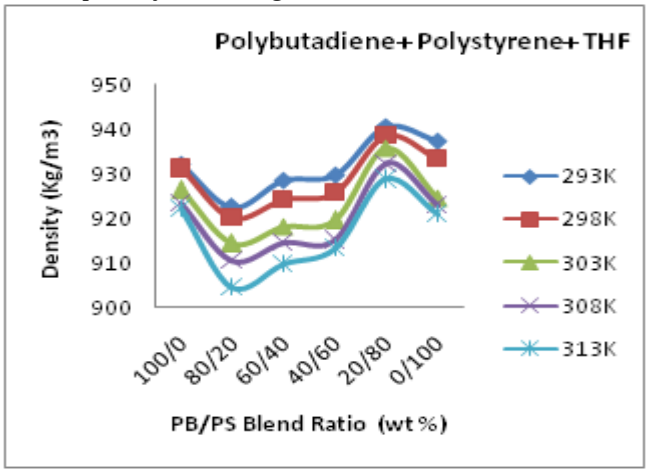

Fig.2

From Fig3 it is clear that adiabatic compressibility shows non-linearity for different blend ratios with respect to temperature 293K-303K for 2MHz. frequency.Adiabatic compressibility results shows opposite trend when compared to results of ultrasonic velocity and density.The decrease in adiabatic compressibility may be due to aggregation of solvent molecules around the solute supporting strong solute-solvent interactions.

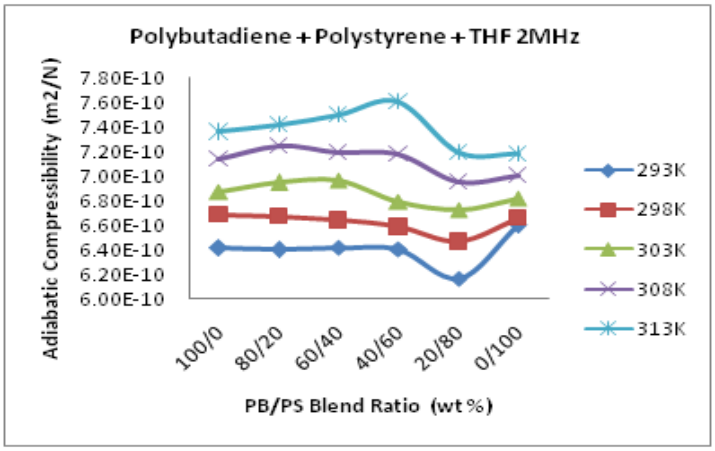

Fig.3

From figure 4 it is clear that free length increases with increase in temperatures at 2MHz frequency. Intermolecular free length shows same behaviour as that of adiabatic compressibility and opposite behaviour as that of ultrasonic velocity. Non-linearity in the free length for different solution blends shows effect of intermolecular forces such as dipole-dipole interactions and dipole induced dipole interactions.

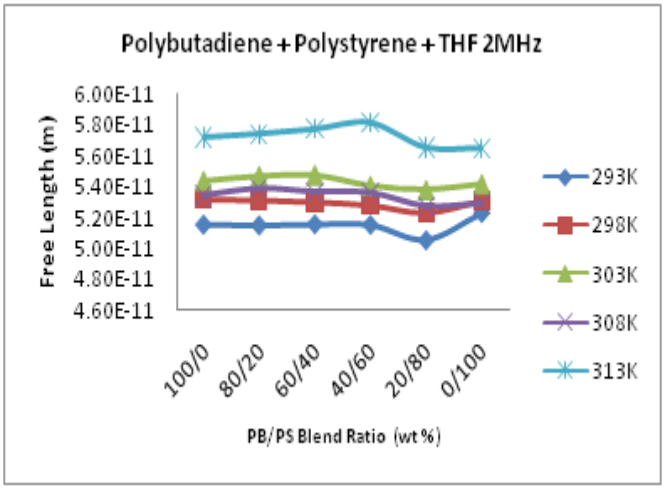

Fig 4

From figure 5 it is clear that Relaxation time decreases with increase in temperature at 2MHz frequency. The variation of relaxation time is cumulative effect of density and ultrasonic velocity. From blend ratio 80/20 to blend ratio 20/80 there is no significant increase or decrease in relaxation time indicating weak interactions in molecules.

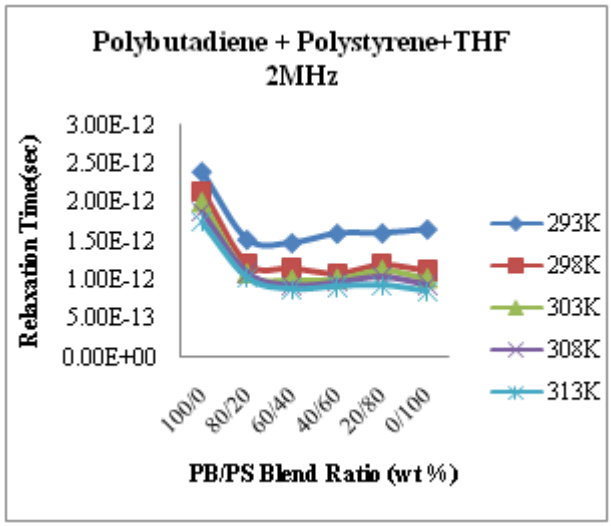

Fig 5

From figure 6 it is evident that Acoustical impedance decreases with increase in temperature at 2MHz frequency. The acoustical impedance is function of elastic property of liquid medium. Acoustical impedance is almost reciprocal of adiabatic compressibility. The increase in acoustical impedance for blend ratio 20/80 confirms presence of molecular association and strong interactions between solute and solvent molecules.

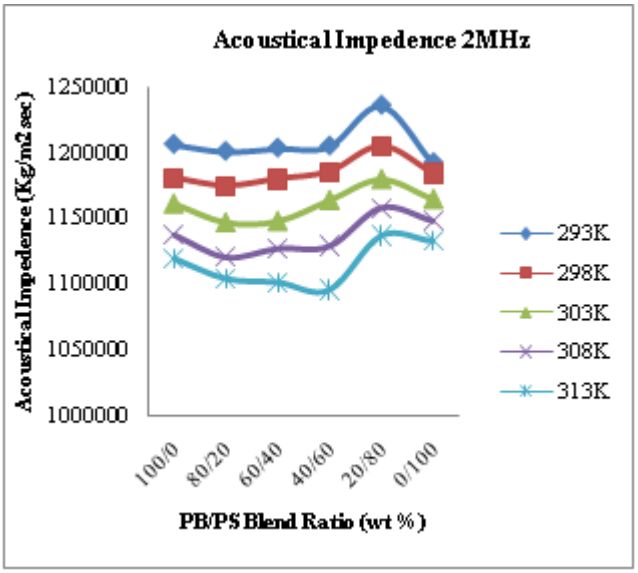

Figure 6

5. Conclusions

1) Thermoacoustical parameters are temperature dependent and also depend on blend ratios in solution.
2) The measurement of thermoacoustical parameters such as ultrasonic velocity, density, adiabatic compressibility, free length, relaxation time and acoustical impedance indicates strength of molecular interactions in polymer blends with various blend ratios.
3) The non-linearity of acoustical parameters for different solution blends confirms presence of polymer-polymer, polymer-solvent interactions and also complex formation and immiscibility.

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