

## VISCOMETRIC, ULTRASONIC, REFRACTOMETRIC AND FTIR STUDIES OF POLY (METHYL METHACRYLATE) / NITROCELLULOSE BLENDS

C. Roumana<sup>a\*</sup> and P.E. Akilandeswari<sup>b</sup>

<sup>a</sup>Department of Physics, Holy Cross College, Trichy - 2.

<sup>b</sup>Department of Physics, J.B.A.S. College for Women, Chennai-18.

\*Corresponding Author Email: [roumana\\_cmi@rediffmail.com](mailto:roumana_cmi@rediffmail.com)

### ABSTRACT

Miscibility studies of Poly (methyl methacrylate) (PMMA) and Nitrocellulose (NC) in common solvent ethyl methyl ketone have been carried out in different percentages of the polymer components in the blend solutions. The interaction parameters have been obtained using the viscosity data to probe the miscibility at 30°C. The ultrasonic velocity, thermo acoustic parameters, excess thermo acoustic parameters and refractive index have been measured for the blends of PMMA/NC and the specific interactions of the blends are identified. The FTIR analysis is carried out for the vibrational characteristics of the samples.

### KEY WORDS

Poly (methyl methacrylate); Nitrocellulose; Viscosity; Ultrasonic velocity; Interactions; Miscibility.

### 1.0. INTRODUCTION

The blending of polymers is one of the simplest means to obtain a variety of physical and chemical properties from the constituent polymers. The gain in newer properties depends on the degree of compatibility or miscibility of polymers at a molecular level. There have been various techniques to study the miscibility of the polymer blends [1, 2, and 3].

Polymer-polymer interactions are generally considered as a result of specific interactions between the polymer segments. The specific interactions capable of inducing polymer miscibility include dipole-dipole interactions, ion-dipole interactions, hydrogen-bond, acid-base reaction, charge transfer etc [4, 5]. The study of molecular interactions was attempted by many experimental techniques. The complete understandings of the nature of inter and intramolecular interactions are not possible by

any single method. Many workers have used viscosity methods to determine polymer-polymer miscibility [6] [7]. The principle of using dilute solution viscosity to measure the miscibility characterisation are based on the fact that, while in solution, molecules of both components may exist in a molecularly dispersed state and undergo a mutual attraction or repulsion which will influence the viscosity[8].

The advantage of using ultrasonic velocity measurements for investigating polymer-polymer interactions has been shown by many workers [9, 10]. This lies in the fact that the basis of viscosity is the basis of ultrasonics for dilute solutions. Chee [11], Sun. et al., [12] and Jiang and Han [13] have suggested the viscometric method for the study of polymer-polymer interactions. Gautam kumar sah et.al., [14] have suggested the use of ultrasonic velocity. Paladhi and Singh [15] have established that the variation of ultrasonic

velocity and viscosity with blend composition as an effective parameter for polymer-polymer interaction. Recently, Varadarajulu et al., [10] have employed the ultrasonic and refractometric techniques for the study of polymer-polymer interactions. In the present investigation, the dilute solution viscosity, ultrasonic and refractometric techniques are employed to investigate and establish the molecular interactions of solute-solute and solute-solvent in the blends of Poly (methyl methacrylate) and Nitrocellulose in the common solvent ethyl methyl ketone at ambient temperature 303 K. An attempt is made to identify the groups that will involve in interactions by FTIR analysis.

## 2.0. MATERIALS AND METHODS

The poly (methyl methacrylate) (PMMA) of molecular weight 98000 is Polymerised from the methyl methacrylate supplied by S.D. fine chemicals, India and the Nitrocellulose of molecular weight 60000 manufactured by Ashahi chemical Industry, Japan have been employed in the present study. 1%w/v binary solutions of PMMA and NC in common solvent ethyl methyl ketone were prepared. Using the binary solutions, the blends of different compositions 8:2, 7:3, 6:4, 5:5, 4:6, 3:7 and 2:8 were prepared. The relative viscosities were measured using an ubbelohde suspended level viscometer for the binary solutions and blends of PMMA/NC. The ultrasonic velocity measurements were performed by an ultrasonic interferometer operating at frequency 2MHz. The densities of the solutions were measured using 10ml standard specific gravity bottle. The refractive indices were measured with Abbe's refractometer. The temperature is maintained at 303K by a thermostat, with a thermal stability of  $\pm 0.05^\circ\text{C}$ . Films were cast on quartz plate out of 1%w/v solutions and polyblends of PMMA/NC. The complete vacuum dried cast films were

employed. The spectra were recorded using Nicolet 20 DXB FTIR spectrophotometer.

## 2.1. Theory

### 2.1.1. Viscometric Analysis

Based on additive law Huggins equation expresses the specific viscosity as a function of concentration if one of the components is alone in solution [8],

$$\eta_{\text{spe}}/C = [\eta] + K_H[\eta]^2 C \quad (1)$$

Where  $[\eta]$  is the intrinsic viscosity,  $\eta_{\text{spe}}/C$  is the specific viscosity at concentration C, and  $K_H$  is the Huggins constant. If  $K_H[\eta]^2 = b$ , where b is the interaction coefficient, then eq. (1) becomes

$$\eta_{\text{spe}}/C = [\eta] + bC \quad (2)$$

Chee [11] extended the Huggins equation for a ternary system of solute A and solute B in common solvent and gave the interaction parameter

$$\Delta B = \frac{\bar{b} - b}{2W_2W_3} \quad (3)$$

$$\text{Where } \bar{b} = W_2b_{22} + W_3b_{33}$$

$$\text{and } \mu = \Delta B / \{([\eta]_2 - [\eta]_1)^2\} \quad (4)$$

The parameter  $\Delta B$  can be used to predict solute-solute interaction in general. Where,  $b_{22}$ ,  $b_{33}$  and  $b_{23}$  are the interaction parameters of the two polymer solutions and blends respectively.  $[\eta]_1$  and  $[\eta]_2$  are the intrinsic viscosities for the pure component solutions. The blend is miscible if  $\mu \geq 0$  and immiscible when  $\mu < 0$ .

Sun. et al., [12] suggested a new criterion, ' $\alpha$ ' based on the classical Huggins equation and Huggins coefficient  $K_m$  in the blends. According to Sun. et al, [12] for a ternary system, there are three types of interaction that might contribute to the value of  $K_m$ ; long-range hydrodynamic interaction of pairs of single molecules given by  $K_{m1}$ ; the formation of double molecules given by  $K_{m2}$ ; and intermolecular attraction or repulsion given by  $K_{m3}$ . Thus, the overall  $K_m$  turns out to be:

$$K_m = K_{m1} + K_{m2} + K_{m3} \quad (5)$$

In the absence of strong special interactions that would encourage aggregation, and at sufficiently low concentrations, the second term  $K_{m2}$  can be neglected. Reabbreviating,  $K_{m3}$  as  $\alpha$  and rearranging the final equation then yields.

$$\alpha = K_m - K_{m1} \quad (6)$$

$$\alpha = K_m - \left[ \frac{K_A [\eta]_A^2 W_A^2 + K_B [\eta]_B^2 W_B^2 + 2\sqrt{K_A K_B} [\eta]_A [\eta]_B W_A W_B}{\{[\eta]_A W_A + [\eta]_B W_B\}^2} \right] \quad (7)$$

Where,  $K_m$  is the experimentally obtained Huggins constant. The parameter  $\alpha$  indicates the nature and strength of the intermolecular interaction. As a criteria the sign of the parameter  $\alpha$  can be used to predict the interactions,  $\alpha \geq 0$  claims solute-solute interaction and  $\alpha < 0$  indicates blend-solvent interaction.

Jiang and Han [13] revised Sun's criterion by substituting an expression for total interaction existing in the system  $K_m$ , illustrated as in equation (7).

$$K_m = \frac{K_A [\eta]_A^2 W_A^2 + K_B [\eta]_B^2 W_B^2 + 2K_{AB} [\eta]_A [\eta]_B W_A W_B}{\{[\eta]_A W_A + [\eta]_B W_B\}^2} \quad (8)$$

Then the new criterion  $\beta$  for the resultant interaction

$$\beta = \frac{2\Delta K [\eta]_A [\eta]_B W_A W_B}{(W_A [\eta]_A + W_B [\eta]_B)^2} \quad (9)$$

$$\text{Where } \Delta K = K_{AB} - (K_{AA} K_{BB})^{\frac{1}{2}}$$

The criteria  $\beta \geq 0$  indicates solute-solute interactions and  $\beta < 0$  is for blend-solvent interactions.

### 2.1.2. Ultrasonics Studies

Ultrasonic velocity ( $u$ ) and density ( $\rho$ ) are the observed parameters. These parameters were employed to calculate some of the thermo acoustic parameters.

i) Adiabatic Compressibility

$$\beta = 1/\rho u \quad \text{m}^2/\text{N} \quad (10)$$

ii) Acoustic impedance

$$Z = \rho u \quad \text{Kgm}^{-2}\text{s}^{-1}. \quad (11)$$

iii) Free length

$$L_f = K \sqrt{\beta} \quad \text{\AA} \quad (12)$$

Where  $k = 93.875 + 0.345 * T * 10^{-8}$ ,  $T$  is the absolute temperature.

$$\text{iv) Free Volume } V_f = \left[ \frac{M_{eff} u}{\eta K} \right]^{\frac{3}{2}} \text{m}^3 \text{mol}^{-1} \quad (13)$$

$$\text{v) Internal Pressure } \pi_i = bRT \left[ \frac{K\eta}{u} \right]^{\frac{1}{2}} \left[ \frac{\rho^{\frac{2}{3}}}{M_{eff}^{\frac{7}{6}}} \right] \text{N/m}^2 \quad (14)$$

Where,  $b$  stands for cubic packing factor which is assumed to be 2 for all liquids and solutions.  $K$  the temperature dependent constant  $4.29 \times 10^9$ ,  $R$  the gas constant,  $T$  the absolute temperature,  $\eta$  the viscosity in  $\text{Nsm}^{-2}$ ,  $u$  the ultrasonic velocity in  $\text{m/sec}$  and  $\rho$  the density in  $\text{Kgm}^{-3}$  of the liquid/mixture.

vi) Excess Parameter  $A^E = A_{\text{expt}} - A_{\text{ideal}}$

$$E = A_{\text{expt}} - \left[ \sum_{i=1}^n x_i A_i \right] \quad (15)$$

Where  $A_{\text{expt}}$  represent the acoustic parameter of the mixture,  $A_i$  represent the acoustical parameter of the pure component  $i$  and  $x_i$  is the corresponding weight fraction. Based on the above relation the following excess acoustic parameters for the blends are calculated.

## 3.0. RESULTS AND DISCUSSIONS

### 3.1. Viscometric Analysis

#### 3.1.1. Analysis of 1%w/v polymer binary solutions

The Huggins plot are drawn  $\eta_{\text{spe}}/C$  Vs concentration  $C$  for 1%w/v solutions of Poly(methyl methacrylate) (PMMA) and Nitrocellulose (NC) in common solvent ethyl methyl ketone (EMK) and blends of PMMA/NC at compositions 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, and 2:8 at temperature 303K are shown in Figure 1. The values of the measured parameters such as, interaction parameter  $b$ , intrinsic viscosity  $[\eta]$ , Huggins constant  $K_H$ , and the derived parameters, the Chee's parameter  $\mu$ , Sun et al., parameter  $\alpha$ , and Jiang and Han's parameter  $\beta$  at temperature 303K are summarized in Table I.

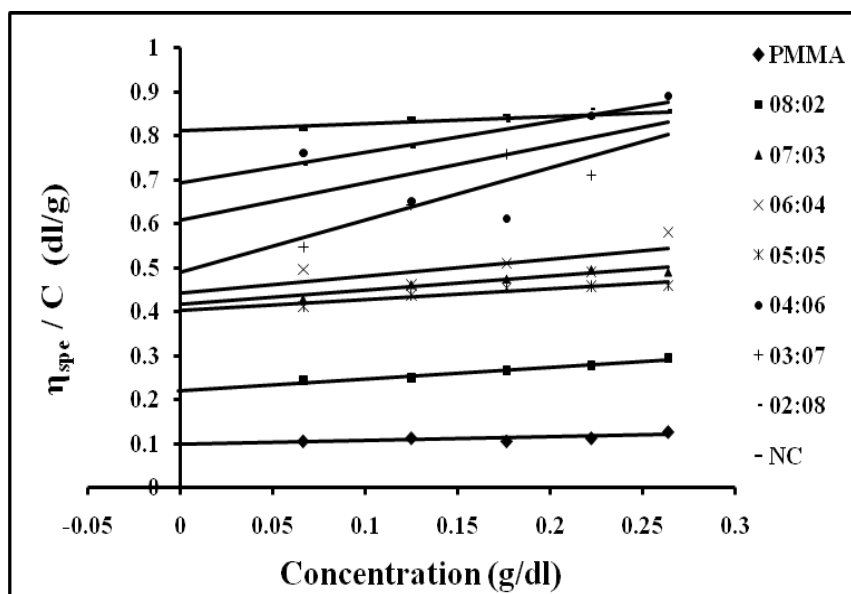


Figure 1 Variation of  $\eta_{spe}/C$  with concentration at 303K

In the present investigation the plot of  $\eta_{spe}/C$  Vs  $C$  of the 1%w/v binary solutions of NC and PMMA give a straight line with an intercept and gradient. For the binary solutions of PMMA and NC, the interaction parameter  $b$  and the intrinsic viscosity  $[\eta]$  are positive. This suggests the probable interaction between the interacting groups of the systems and this leads to the solubility of the solute in the solvent.

The higher value of  $[\eta] = 0.8111$  obtained in NC solution confirms the existence of high degree of interactions between the molecules of ethyl methyl ketone and nitrocellulose. This is in agreement with the reported observation [15].

Table I: The observed and calculated viscometric parameters of the blends of PMMA/NC at 303K

Compositions	[ $\eta$ ] Intrinsic viscosity dl/g	$K_H$ Huggins constant	Interaction parameters			
			$b$	$\mu$	$\alpha$	$\beta$
PMMA	0.1	8.08	0.0808			
08:02	0.2293	3.180	0.1672	0.126	1.557	0.7776
07:03	0.4161	1.863	0.3226	0.568	0.815	0.1530
06:04	0.4427	1.948	0.3818	0.736	1.198	0.1385
05:05	0.4023	1.517	0.2456	0.349	0.944	0.0186
04:06	0.608	2.285	0.8447	2.052	1.825	0.1211
03:07	0.4889	4.971	1.1883	3.029	4.590	0.3384
02:08	0.6933	1.444	0.6942	1.625	1.119	0.0013
NC	0.8111	0.250	0.1647			

### 3.1.2. Analyses of PMMA/NC blend system

At all compositions, the interaction parameter  $b$  gives a positive value and indicates the domination of polymer-polymer interactions. The positive value of  $K_H$  indicates the attractive interactions and the negative value indicate the repulsive interaction among the polymeric molecules [16].

The Chee's criteria  $\mu \geq 0$ , the Sun. et al. criteria  $\alpha \geq 0$  and the improved parameter criteria  $\beta \geq 0$  for polymer-polymer interactions are satisfied at all compositions with the observed positive values of  $\mu$ ,  $\alpha$ , and  $\beta$ . This observation confirms the miscibility in the blends of PMMA/NC at 303K.

This result is in agreement with the reported results in the blends of SBR/PMMA [17], PMMA/CAB [18], PVC/PMMA [10] and PVA/PMMA [19].

### 3.2. Thermo acoustical investigations

#### 3.2.1. Thermo acoustical investigation of 1%w/v Polymer solutions

The measured parameter of ultrasonic velocity  $u$  and the derived thermo acoustic parameters, adiabatic compressibility  $\kappa$ , and the free length  $L_f$  for the pure solvent ethyl methyl ketone and 1% polymer solutions of PMMA and NC were discussed in Table II.

**Table II: The derived and observed thermo acoustic parameters of the blends of PMMA/NC at 303K**

Compositions	Ultrasonic velocity m/s	Density Kgm <sup>-3</sup>	Acoustic Impedance 10 <sup>-5</sup> Nsm <sup>-3</sup>	Adiabatic Compressibility 10 <sup>10</sup> m <sup>2</sup> /N	Free Length Å	Viscosity Nsm <sup>-2</sup> 10 <sup>4</sup>	Free Volume 10 <sup>3</sup> m <sup>3</sup> mol <sup>-1</sup>	Internal Pressure 10 <sup>-6</sup> N/m <sup>2</sup>	Refractive index
PMMA	1197.6	793.6	9.500	8.7898	0.5882	7.9053	4.0758	1.5425	1.376
8:2	1195.4	794.0	9.470	8.8336	0.5897	6.5479	5.4118	1.3998	1.378
7:3	1215.8	793.6	9.633	8.5386	0.5798	6.1373	6.1286	1.3420	1.377
6:4	1217.0	793.3	9.646	8.5183	0.5791	6.0709	6.2502	1.3325	1.382
5:5	1224.6	793.2	9.714	8.4068	0.5753	5.2600	7.8372	1.2353	1.382
4:6	1230.0	792.6	9.758	8.3321	0.5727	4.9468	8.6661	1.1937	1.378
3:7	1233.4	792.3	9.788	8.2831	0.5710	4.4753	10.1320	1.1324	1.382
2:8	1251.6	792.2	9.938	8.0399	0.5626	4.2258	11.3090	1.0912	1.381
NC	1332.5	793.2	1.057	7.0968	0.5286	3.7770	14.7560	0.9966	1.381

For 1%w/v PMMA and NC solutions, the ultrasonic velocity increases to  $u=1197.6$  m/s and  $u=1332.5$  m/s and adiabatic compressibility decreases to  $8.7898 \times 10^{-10}$  m<sup>2</sup>/N and  $7.097 \times 10^{-10}$  m<sup>2</sup>/N from the values of the solvent EMK  $u = 1164.0$  m/s and  $\kappa = 9.3048 \times 10^{-10}$  m<sup>2</sup>/N. The increase in ultrasonic velocity and decrease in adiabatic compressibility indicates the salvation/hydration behaviour of the solute in the solvent. It is reported that the adiabatic compressibility of the solution is found to be less than that of pure solvent due to salvation/hydration [20]. The observed values of

free length show a decrease with respect to the pure solvent EMK. The decrease of  $L_f$  is attributed to the close packing of molecules and that the solute dissolves in the solvent [20]. From the behaviour of the above thermo acoustic parameters it is evident that the polymer molecules are dispersing in the solvent effectively.

#### 3.2.2. Thermo acoustical analysis of PMMA/NC blends systems

The values of the measured and derived acoustical parameters of the PMMA/NC blend system at the compositions 8:2, 7:3, 6:4, 5:5, 4:6,

3:7 and 2:8 in general show a linear behaviour. The values of the parameters are summarized in

Table II and the behavioural graphs are shown in Figures 2, 3 and 4.

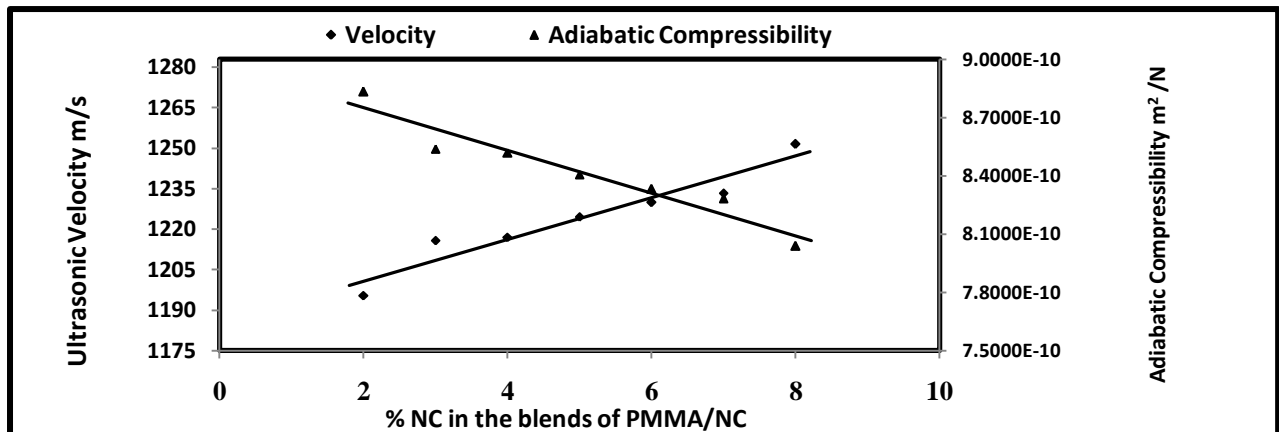


Figure 2 Variation of ultrasonic velocity and adiabatic compressibility with PMMA/NC blend compositions at 303K

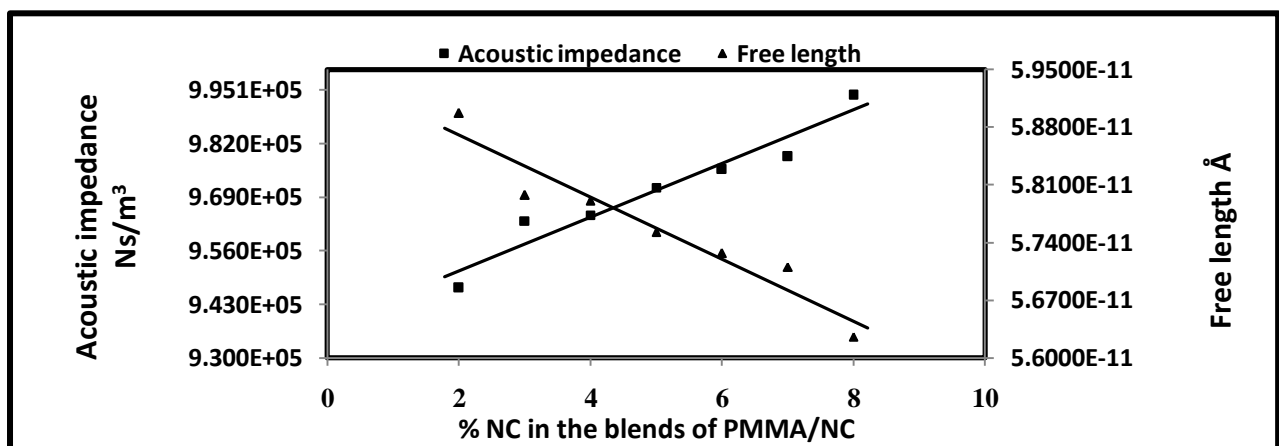


Figure 3 Variation of acoustic impedance and free length with PMMA/NC blend compositions at 303K

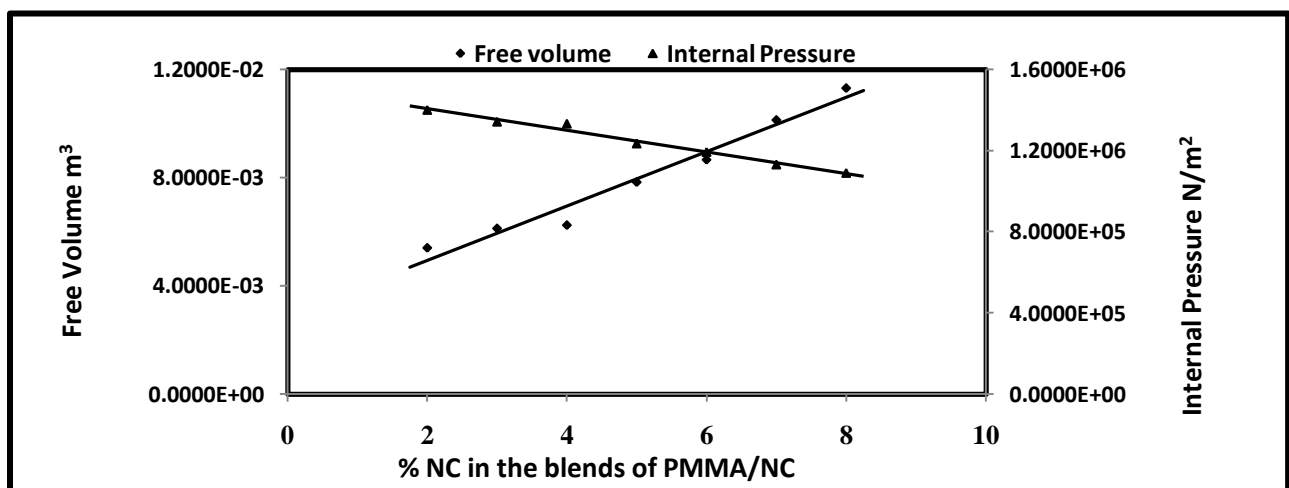


Figure 4 Variation of Free volume and internal pressure with PMMA/NC blend compositions at 303K

In general the parameters show a linear behaviour with compositions. Gautam kumar sah et al., [14] have pointed out that the behaviour of  $u$  and  $\rho$  with blend composition is linear for miscible blends, whereas the curves depicting this variation for immiscible blends are found to have S or inverted S shapes. The observed linear increase in ultrasonic velocity  $u$ , density  $\rho$  and viscosity  $\eta$  with compositions indicates that the blends are miscible. These results were similar to the observation of Varadarajulu et al, [21] in the study of PVP-PS blends in a mixed solvent of dimethyl formamide and cyclohexanone. Paladhi and Singh [1] observed the linear variation of ultrasonic velocity and viscosity with blend compositions in the case of PMMA/PVAc.

According to Gautam kumar sah et al, [14] and Sidkey et al., [22] the presence of one maximum reflects the mutual solubility of the polymeric components in the polyblends. They also reported that more than one maximum indicate the presence of phase inversion in the blend system [23]. Further, the linear variation of measured thermo acoustical parameters were also effectively reveals the miscible nature of the polymers in the blend system. The observed linear relationship between the acoustic impedance and the ultrasonic velocity indicates strong solute-solute interactions. The linear

behaviour of free length  $L_f$  decreases with increase in acoustic impedance  $z$  was observed [24].

V. Arumugam et al., [17] in the study of SBR: PMMA blend system had showed the linear increase in ultrasonic velocity  $u$ , the adiabatic compressibility  $\kappa$ , viscosity  $\eta$  and free volume  $V_f$ , whereas the internal pressure  $\pi_i$  decreases linearly with PMMA compositions. Such behaviour is observed in the present investigation of acoustical parameters. The free volume  $V_f$  and the internal pressure  $\pi_i$  maintain an inverse relationship between them. The linear behaviour of  $V_f$  and  $\pi_i$  reveals the presence of solute-solute interaction in the blend system [17].

The thermo acoustical parameters of PMMA/NC blends at compositions establish the existence of polymer-polymer interaction in the blend system. The confirmation of such interaction through excess parameters is possible as they are capable of giving more insight of intermolecular interactions.

### 3.2.3. Analysis of Excess parameters in PMMA/NC system

The excess properties of acoustical parameter of PMMA/NC blends are summarized in Table III and their behaviours are plotted against composition in figures 5, 6, 7 and 8. The excess parameters exhibit a nonlinear variation with compositions.

**Table III: The derived excess thermo acoustic parameters of the blends of PMMA/NC at 303K**

Compositions	Excess Ultrasonic velocity $m/s \cdot 10^{-1}$	Excess Acoustic Impedance $10^{-4} Nsm^{-3}$	Excess Adiabatic Compressibility $10^{11} m^2/N$	Excess Free Length $10^{12} \text{Å}$	Excess Free Volume $10^3 m^3 mol^{-1}$	Excess Internal Pressure $10^{-4} N/m^2$	Excess Viscosity $Nsm^{-2} \cdot 10^5$
8:2	-2.9180	-2.4476	3.8244	1.3396	-0.800	-3.3510	-5.3174
7:3	-2.2270	-1.8943	2.5671	0.9434	-1.151	-3.6715	-5.2951
6:4	-3.4560	-2.8352	4.0573	1.4712	-2.098	0.8380	-1.8308
5:5	-4.0450	-3.2368	4.6347	1.6880	-1.579	-3.4225	-5.8115
4:6	-4.8540	-3.8712	5.5806	2.0288	-1.818	-2.1230	-4.8152
3:7	-5.8630	-4.6395	6.7835	2.4566	-1.420	-2.7935	-5.4019
2:8	-5.3920	-4.2200	6.0445	2.2084	-1.311	-1.4540	-3.7686

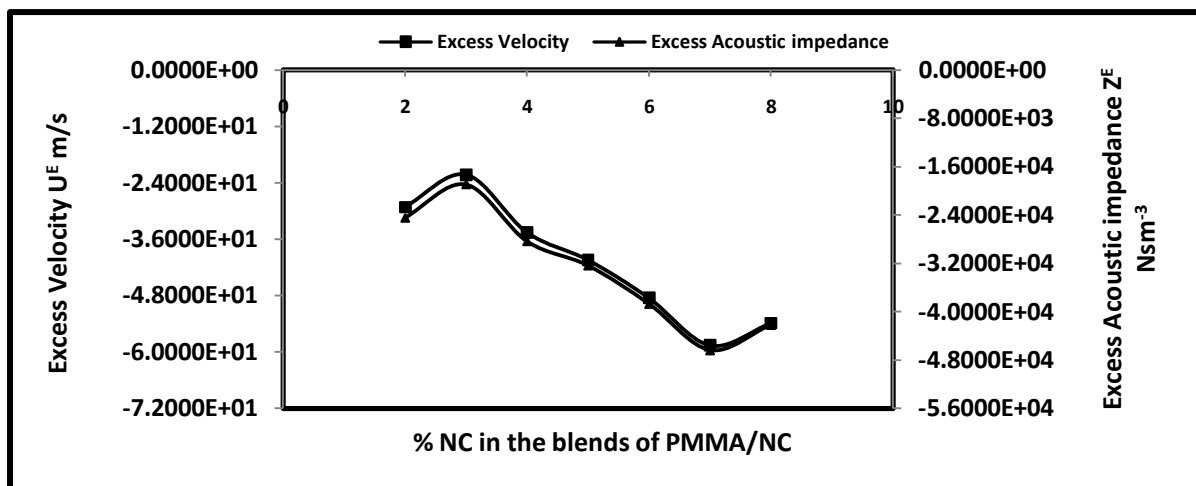


Figure 5 Variation of  $U^E$  and  $Z^E$  with PMMA/NC blend compositions at 303K

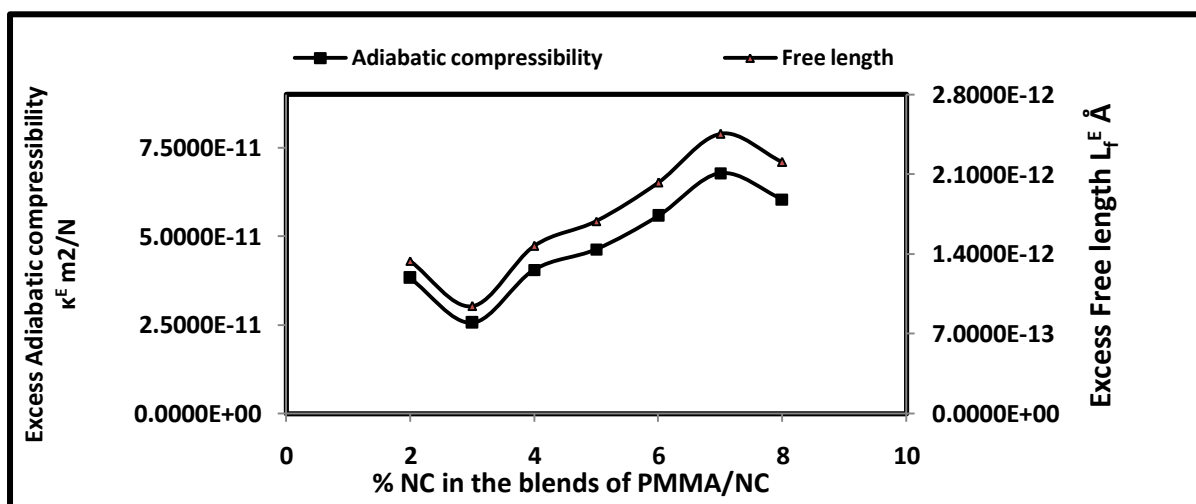


Figure 6 Variation of  $\kappa^E$  and  $L_f^E$  with PMMA/NC blend compositions at 303K

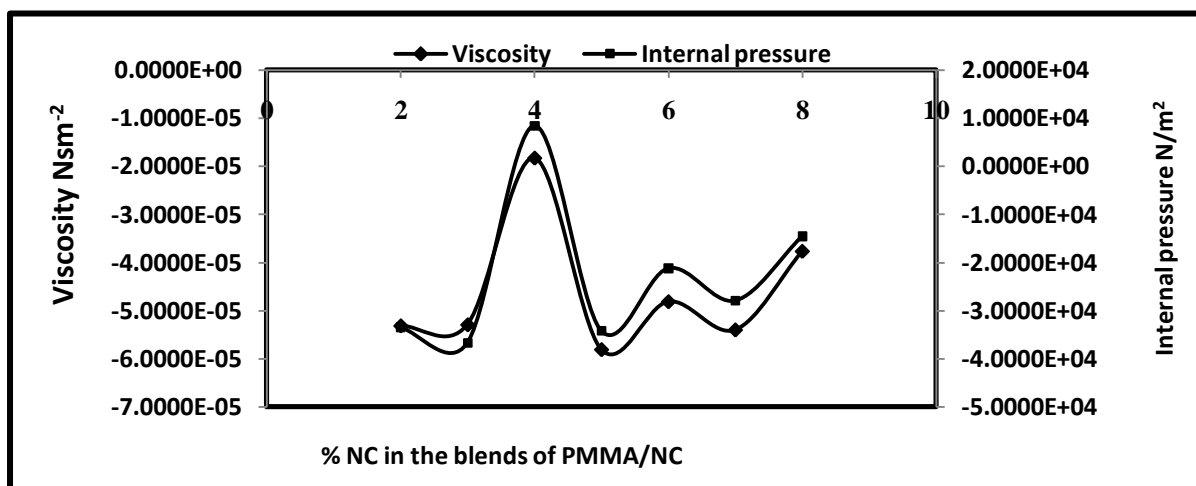


Figure 7 Variation of  $\eta^E$  with PMMA/NC blend compositions at 303K



The excess ultrasonic velocity  $u^E$  and the excess acoustic impedance  $z^E$  are negative. The negative values of these parameters indicate decreasing strength of interaction between the component molecules and such observations are in agreement with the observation of Vasantharani et al., [25]. The positive excess adiabatic compressibility  $\kappa^E$  suggests loosely packed molecules in the mixture due to the difference in size and shape of the molecules [26]. In the

present investigation, the excess intermolecular free length  $L_f^E$  is positive with negative excess acoustic impedance  $z^E$ , while the positive  $L_f^E$  suggests loosely packed molecules in the mixture. The behaviours of  $L_f^E$  and  $z^E$  suggest that in addition to dipole-dipole and dipole-induced dipole interactions, dispersion forces are also operative in the blend system. The dispersive forces make a positive contribution to  $L_f^E$  while the negative contribution to  $z^E$  [27] [28].

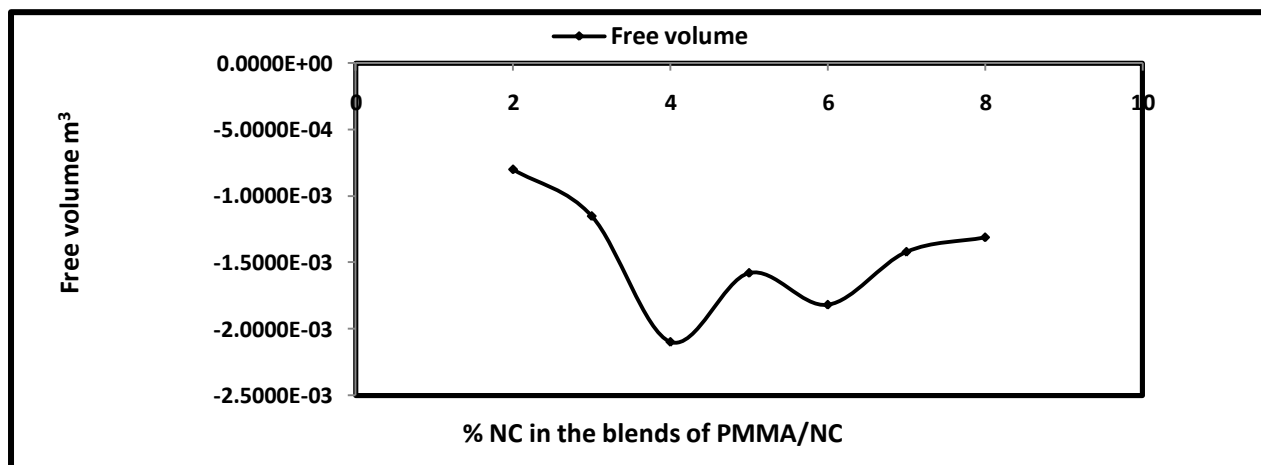


Figure 8 Variation of  $V_f^E$  with PMMA/NC blend compositions at 303K

The negative excess viscosity  $\eta^E$  property is exhibited at all compositions. The negative  $\eta^E$  is generally attributed to the dipolar forces between the component molecules [29]. The negative excess viscosity may be explained by considering the factors such as (i) The difference in size and shape of the molecules and (ii) The loss of dipolar association in pure component. The observed deviation in negative excess viscosity  $\eta^E$  from rectilinear dependence is attributed to the dominance of dispersive forces particularly for the systems having different molecular size [30]. The observed negative values of excess internal pressure  $\pi_i^E$  in an indication of

that only dispersion and dipolar forces are operating [31].

The observed negative excess free volume  $v_f^E$  indicates the presence of intermolecular interaction in the system. The analysis of excess parameters confirms the existence of weak intermolecular interactions among the component of the blend system. The specific interactions like dipole-dipole interaction should be responsible for the miscibility observed between PMMA and NC in solution. The functional sites present in the structure of these polymers can be seen in Figure 9 and 10.

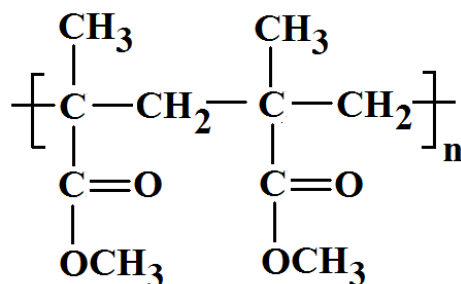


Figure 9 (a, b) Structure of Poly (methyl methacrylate)

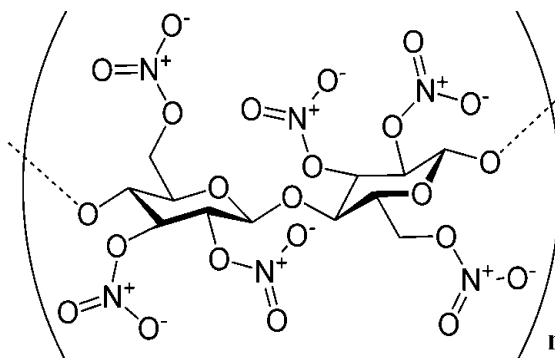


Figure 10 Structure of Nitrocellulose

#### 4.0. REFRACTOMETRIC TECHNIQUE

The measured refractive index of the blends of PMMA/NC were summarized in Table II. The plot of refractive indices against compositions for the

above blend system is shown in Figure 11. The polymer blends after preparation appear to be transparent.

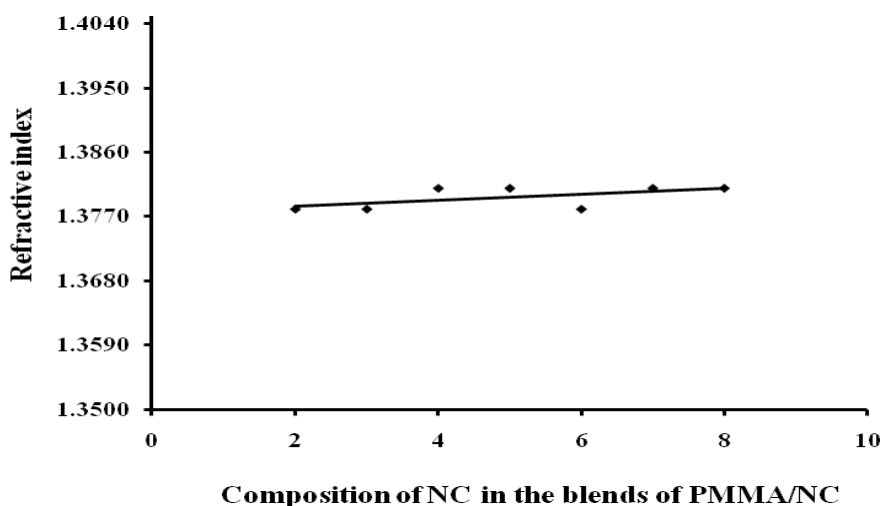


Figure 11 Variation of refractive index with PMMA/NC blend compositions at 303K

From the recorded values of refractive indices of PMMA/NC system, the refractive indices increase

with the increase of Nitrocellulose composition. This linear increase in refractive index is only by

third decimal. The observations made in the present investigation suggest the polymer-polymer interaction in the polymer blend system. The linear variations of refractive index were an indication of polymer-polymer interactions. Varadarajulu et. al., [10][21] in the study of Poly (Vinyl chloride) / Poly (methyl methacrylate) blend and PVP/PS blend system through ultrasonic and refractive index had attributed the linear variation in the refractive index to the single phase of polymer-polymer interaction. The prepared polymer blends of PMMA/NC appear to be transparent indicating possible polymer-polymer interaction [33]. The measurement of refractive index was in conformity with the results obtained by DSV and ultrasonics, where the dominance of polymer-polymer interactions is reported.

#### 5.0. Spectral analysis of PMMA/NC blends

FTIR spectroscopy has been widely used by many researchers to study the formation of blends [34]. The spectra of PMMA/NC blends at different

compositions were shown in Figure 12. The obtained spectra exhibit the characteristic absorption frequencies of prominent groups of PMMA and NC. The absorption frequencies of the active groups in the blends were identified. The broad symmetric absorption bands of hydroxyl with centred frequency are observed at  $3434.7\text{ cm}^{-1}$ ,  $3500.8\text{ cm}^{-1}$ ,  $3432\text{ cm}^{-1}$ ,  $3439\text{ cm}^{-1}$ ,  $3500.9\text{ cm}^{-1}$ ,  $3497.7\text{ cm}^{-1}$  and  $3478.9\text{ cm}^{-1}$  for compositions 8:2, 7:3, 6:4, 5:5, 4:6, 3:7 and 2:8 in PMMA/NC blend system. The OH stretching frequency of 1% NC solution was observed at  $3532\text{ cm}^{-1}$ . It shows the characteristic wide distribution of hydroxyl in the blend as hydroxyl-hydroxyl and hydroxyl-carbonyl bond indicating the hydrogen bonding interaction in the blends. The above observed frequencies indicate equilibrium between hydrogen bonded hydroxyl-absorption and hydrogen bonded carbonyl absorption [35]. Casteres, et al. [36], reported a hydroxyl bond for specific interaction in the polymer blends.

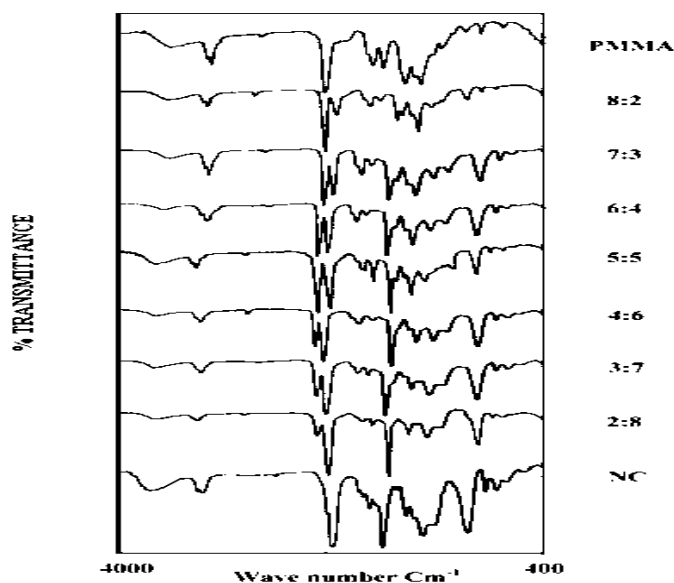


Figure 12 FTIR spectra of PMMA/NC blends at different compositions.

The characteristic carbonyl ester C=O of PMMA exhibit sharp peaks at  $1728.04\text{ cm}^{-1}$ ,  $1729\text{ cm}^{-1}$ ,

$1728.03\text{ cm}^{-1}$ ,  $1729.7\text{ cm}^{-1}$ ,  $1726.56\text{ cm}^{-1}$ ,  $1726.39\text{ cm}^{-1}$  and  $1725.3\text{ cm}^{-1}$  for the compositions 8:2,

7:3, 6:4, 5:5, 4:6, 3:7 and 2:8 where a shift of  $4\text{cm}^{-1}$ ,  $3\text{cm}^{-1}$ ,  $4\text{cm}^{-1}$ ,  $3\text{cm}^{-1}$ ,  $6\text{cm}^{-1}$ ,  $6\text{cm}^{-1}$ ,  $7\text{cm}^{-1}$  are recorded with reference to 1% PMMA ( $\nu_{\text{C=O}}$   $1732\text{cm}^{-1}$ ). The observed shift in carbonyl frequencies may be attributed to the involvement of the carbonyl ester in interaction. Similar shift in carbonyl frequency is observed in Polyester/Nitrocellulose blends by Jean-Jacques Jutier [37] and in the miscibility studies by Shiao Wei Kuo and Feng Chih and Chang [38] and attributed to the carbonyl interactions.

The carbonyl ester interaction in the system is confirmed by the C-O stretching frequencies which splits into two asymmetric stretching frequencies as  $-\text{C}-\text{C}(=\text{O})-\text{O}$  and  $-\text{O}-\text{C}-\text{C}$  and C-C-C bending frequency. In the present system  $-\text{C}-\text{C}(=\text{O})-\text{O}$  frequencies appear at  $1192\text{cm}^{-1}$ ,  $1193\text{cm}^{-1}$ ,  $1188\text{cm}^{-1}$ ,  $1164\text{cm}^{-1}$ ,  $1118\text{cm}^{-1}$  and  $1195\text{cm}^{-1}$ , the O-C-C frequencies appear at  $1064.5\text{cm}^{-1}$ ,  $1067.78\text{cm}^{-1}$ ,  $1067.45\text{cm}^{-1}$ ,  $1067.3\text{cm}^{-1}$ ,  $1067.47\text{cm}^{-1}$ ,  $1067.47\text{cm}^{-1}$ ,  $1068.2\text{cm}^{-1}$  and C-C-C bending frequencies appear at  $1150.2\text{cm}^{-1}$ ,

$1152.99\text{cm}^{-1}$ ,  $1153\text{cm}^{-1}$ ,  $1153\text{cm}^{-1}$ ,  $1155\text{cm}^{-1}$ ,  $1156.49\text{cm}^{-1}$  and  $1157.3\text{cm}^{-1}$  at compositions 8:2, 7:3, 6:4, 5:5, 4:6, 3:7 and 2:8 respectively.

At compositions the sharp absorption peaks of nitrate ester stretching at  $1656.70\text{cm}^{-1}$ ,  $1655.90\text{cm}^{-1}$ ,  $1655.20\text{cm}^{-1}$ ,  $1654.5\text{cm}^{-1}$ ,  $1655.39\text{cm}^{-1}$ ,  $1655.62\text{cm}^{-1}$ ,  $1656.2\text{cm}^{-1}$  are recorded with reference to 1% NC ( $\nu_{\text{C=O}}$   $1652\text{cm}^{-1}$ ) and corresponding bending frequencies are observed at  $666.0\text{cm}^{-1}$ ,  $671.92\text{cm}^{-1}$ ,  $683.8\text{cm}^{-1}$ ,  $666.2\text{cm}^{-1}$ ,  $693.2\text{cm}^{-1}$ ,  $691.8\text{cm}^{-1}$  and  $691.0\text{cm}^{-1}$  and the N-O linkage frequencies at  $842\text{cm}^{-1}$ ,  $842.39\text{cm}^{-1}$ ,  $840.52\text{cm}^{-1}$ ,  $841\text{cm}^{-1}$ ,  $839\text{cm}^{-1}$ ,  $839\text{cm}^{-1}$ ,  $840\text{cm}^{-1}$  for compositions 8:2, 7:3, 6:4, 5:5, 4:6, 3:7 and 2:8 respectively. Through the shift in stretching frequency of nitrate ester is negligible; the presence of N-O linkage indicates the interaction, probably with ester carbonyl with dipole-dipole [39]. The observation leads to the conclusion that nitrate groups prefers dipole-dipole interactions in the blends.

**Table IV: The observed FTIR spectral frequency values of the blends of PMMA/NC at compositions.**

Group	Observed frequencies at compositions $\text{Cm}^{-1}$									
	PMMA	8:2	7:3	6:4	5:5	4:6	3:7	2:8	NC	
OH stretching		3434.7	3500.81	3432.433	3500	3439.1	3500.89	3497.69	3478.9	3645 3532 3419
asymmetric stretching	2990.91	2994.9	2995.05	3000.00	2995.11	3000.00	2995.00	2994.00	2994.00	2978
CH <sub>3</sub> carbonyl ester C=O	2950.15	2951.3	2952.82	2951.15	2951.6	2952.16	2928.00	2926.00	2926.00	1705(1718)
nitrate ester stretching	1732.00	1728.04	1729.06	1728.03	1729.7	1726.56	1726.39	1725.3	1725.3	1652
CH <sub>3</sub> asymmetric bending	1443.38	1443.4	1446.39	1445.70	1443.6	1445.82	1445.54	1436.1	1436.1	1455(1417)
	1380.83	1383.1	1381.64	1381.22	1382.3	1378.96	1375.39	1381.8	1381.8	1374
		1277.9	1280.25	1279.15	1279.3	1279.12	1280.39	1280	1280	
$-\text{C}-\text{C}(=\text{O})-\text{O}$ bending	1242.01	1243.3	1244.95							
	1191.07		1192.37	1192.93	1188	1164	1118	1118	1118	
C-C-C bending	1149.93	1150.2	1152.99	1153.21	1152.6	1155.34	1156.49	1157.3	1157.3	1159(1172)
O-C-C bending	1062.45	1064.5	1067.78	1067.45	1067.3	1067.47	1067.74	1068.2	1068.2	
C-H bending	988.87		993.97	994.59		997.40				
N-O linkage		842.00	842.39	840.52	841	839.11	839.13	840.1	840.1	838
Out of plane C-H bending	750.75	750	750.89	750.54	750.7	750.39	749.93	750.3	750.3	750
NO <sub>2</sub> bending		666.00	671.92	683.824	666.2	693.29	691.82	691	691	693

The asymmetric stretching CH<sub>3</sub> doublet are observed at  $2994.9\text{cm}^{-1}$ ,  $2951.3\text{cm}^{-1}$ ;  $2995.05\text{cm}^{-1}$ ,  $2952.82\text{cm}^{-1}$ ;  $3000\text{cm}^{-1}$ ,  $2951.15\text{cm}^{-1}$ ;

$2995.11\text{cm}^{-1}$ ,  $2951.6\text{cm}^{-1}$ ;  $3000\text{cm}^{-1}$ ,  $2952.16\text{cm}^{-1}$ ;  $2995\text{cm}^{-1}$ ,  $2928\text{cm}^{-1}$  and  $2994\text{cm}^{-1}$ ,  $2926\text{cm}^{-1}$ ; are recorded with reference to 1% PMMA

( $\nu_{C=O}$  2990.91  $\text{cm}^{-1}$ ) and 1%NC ( $\nu_{C=O}$  2978  $\text{cm}^{-1}$ ). The corresponding bending frequencies of asymmetric  $\text{CH}_3$  are 1383  $\text{cm}^{-1}$ , 1443  $\text{cm}^{-1}$ ; 1382  $\text{cm}^{-1}$ , 1446  $\text{cm}^{-1}$ ; 1381  $\text{cm}^{-1}$ , 1446  $\text{cm}^{-1}$ ; 1382  $\text{cm}^{-1}$ , 1444  $\text{cm}^{-1}$ ; 1379  $\text{cm}^{-1}$ , 1446  $\text{cm}^{-1}$ ; 1375  $\text{cm}^{-1}$ , 1446  $\text{cm}^{-1}$  and 1382  $\text{cm}^{-1}$ , 1436  $\text{cm}^{-1}$  at compositions 8:2, 7:3, 6:4, 5:5, 4:6, 3:7 and 2:8 respectively. The group ester carbonyl C=O, methyl  $\text{CH}_3$  of PMMA and the groups ester nitrate  $-\text{O}-\text{NO}_2-$ , Hydroxyl OH involve in interactions in the blend of PMMA/NC at all compositions and their involvement in interactions is well reflected in the FTIR spectrum. These groups show the shift in their stretching frequencies and the stretching is confirmed by their respective bending frequencies. The probable interactions may take place among the groups may be hydroxyl with ester carbonyl and methyl. A dipole-dipole interaction will be favoured between nitrate ester and the ester carbonyl  $\text{C}=\text{O} - \text{O}_2\text{N} - \text{O}$ . In the FTIR investigation of PVC/PMMA blends in THF, Mohamed Saleem Khan et al., [3] have suggested that the carbonyl groups of PMMA involve in interaction. Similarly, Ashok kumar et. al., [40] have clearly explained the miscibility of the polymers in their studies.

### CONCLUSIONS

The interaction behaviour of Poly (methyl methacrylate) and Nitrocellulose in a common solvent of ethyl methyl ketone can be explained on the basis of their molecular structure. The individual polymers had established a good solubility in the polymeric solution in the blend system. The interaction parameter  $b$  and  $[\eta]$  in the solutions and blend with the positive values suggested the interaction between the groups that were present in the system. The Chee's parameter  $\Delta B$ ,  $\mu$ ,  $\alpha$  and  $\beta$  indicates the dominance of solute-solute/polymer-polymer interactions which were specific in nature. The conformity of interactions exhibited by the

viscometric technique was obtained from the linear behaviour of thermo acoustic parameters. The dominant of solute-solute interactions which result by the dipole-dipole interactions were proclaimed by excess thermo acoustic parameters. The linear behaviour of refractive index claims the homogenous nature of the blend systems. Therefore there was only single phase formation in the blend system. The FTIR analysis of PMMA/NC blends identify that the groups carbonyl C=O, methyl  $\text{CH}_3$  of PMMA and nitrate  $-\text{O}-\text{NO}_2-$ , hydroxyl OH of NC were involved in interaction to form the miscible polymer blends.

### REFERENCES

1. Paladhi R, Singh RP. Miscibility and interaction studies on some aqueous polymer blend solutions by ultrasonic and rheological techniques, *J. App.Polym.Sci* 1994, 51, 1559-1565.
2. G.S. Guru, P. Prasad, HR. Shivakumar and S. K. Rai, Miscibility, thermal and mechanical studies of methylcellulose/poly (vinyl alcohol) blends, *IJRPC* 2012, 2(4).
3. Mohammad Saleem Khan, Raina Aman Qazi and Mian Said Wahid, Miscibility studies of PVC/PMMA and PS/PMMA blends by dilute solution viscometry and FTIR, *African Journal of Pure and Applied Chemistry* 2008, 2 (4), 041-045.
4. Olabisi, O., Robekson, L.M. and Shaw, M.T., "Polymer-Polymer Miscibility", Academic Press, Chur, Switzerland, 1982, 68(6), 1-711.
5. G. S. Guru, P. Prasad, H. R. Shivakumar, S. K. Rai, Studies on the compatibility of Pullulan-carboxymethyl cellulose blend using simple techniques, *Malaysian Polymer Journal (MPJ)* 2008, 3(2), 13-23.
6. Ayse Z. Aroguz, Yasemin Kismir, Viscometric study on the miscibility of polystyrene/brominated polystyrene blends, *Eur.Polym. J.*, 2007, 43, 410-415.
7. Moriyuki Sato, Tomohiro Koshino, Yasuko Kajitani, Isamu Inamura, Yasuo Kubo, Miscibility study of polymer blends composed of semirigid thermotropic liquid crystalline polycarbonate,

- Poly (Vinyl alcohol) and chitosan, *J. Appl. Polym. Sci.*, 2004, 93, 1616-1622.
8. M.L. Miller, *The structure of Polymers*, Reinhold book corporation, New York 1966.
  9. S. Rajagopalan and S.J. Sharma, study of mulberry silk-polyacryl amide blend using ultrasonic technique, *J. Pure Appl. Ultrason.* 2005, 27, 105-109.
  10. A. Varada Rajulu, R. Lakshminarayana reddy, S. M. Raghavendra, S. Akheel Ahmed, Miscibility of PVC/PMMA blend by the ultrasonic and refractive index method, *Eur. Polym J.*, 1999, 35, 1183-1186.
  11. K. K. Chee, Determination of polymer-polymer miscibility by viscometry, *Eur. Polym. J.* 1990, 26 (4), 423-426.
  12. Zhi nhua Sun, Wei Wang and Zhiliu Feng, Criterion of polymer-polymer miscibility determined by viscometry, *Eur. Polym. J.*, 1992, 28, 1259-1261.
  13. Jiang, W.H., Han, S. J., An improved criterion of polymer-polymer miscibility determined by viscometry, *Eur. Polym. J.* 1998, 34, 1579-1584.
  14. Gautham kumar sah, Ashok kumar gupta, Miscibility studies of PVC/PMMA blends tetrahydrofuran by viscosity, density, refractive index and ultrasonic velocity method, *Nanosystems: Physics, Chemistry, Mathematics*, 2013, 4(2), P.288-293.
  15. Leopold Schefflan and Morries, B. Jacob, *The Hand Book of Solvents*, D. Van Nostrand company Inc., New York, 1953, 1-280.
  16. Isamu Inamura, Makoto Kittaka, Tatsuya Aikou, Kazuhiko Akiyama, Tomoyuki Matsuyama, Masatsugu Hiroto and Ken-ichi Hirade, Relation between Huggins constant and compatibility of binary polymer mixtures in the aqueous ternary systems, *macromol. Res.*, 2004, 12 (2), 246-250.
  17. V. Arumugam, M.D. Naresh, R. Balakrishnan, R. Sanjeevi, K. Pradeepa and K. Jayakumar, Ultrasonic studies on the blends of styrene butadiene rubber with PMMA and PVAC, *J. Pure Appl. Ultrason.* 2005, 27, 1-7.
  18. M. Selvakumar and D. Krishna Bhat, Miscibility of Poly (methyl methacrylate) and cellulose acetate butyrate blend in dimethyl formamide, *Ind. J. Chem. Technol.*, 2008, 15, 547-554.
  19. Yang Haiyang, Zhu Pingping, Ren feng, Wang yuanyuan, Zhang Tiao, Viscometric investigations on the intermolecular interactions between Poly (methyl methacrylate) and Poly (vinyl acetate), *Eur. Polym. J.*, 2000; 36: 21-26.
  20. Kalyanasundaram, S., Sundaresan, B. And Hemalatha, J., salvation study of polymer by ultrasonic method, *J. Polym. Mater.* 2000, 17, 155- 163.
  21. A. Varada Rajulu, R. Lakshminarayana Reddy, Siddaramaiah, Ultrasonic, Refractometric, and viscosity studies of some polymer blends in solution, *J. Appl. Polym. Sci.*, 1998, 70, 1823-1827.
  22. M. A. Sidkey, A. M. Abd El Fattah, N. S. Abd El AllN. Somanathan, A. Sanjay, Compatibility studies on some solutions of rubber blends by ultrasonic techniques, *J. Appl. Polym. Sci.*, 1992, 46 (4), 581 – 585.
  23. V. Arumugam, *J. App. Polym. Sci.*, Compatibility studies on polystyrene and poly-n-butyl methacrylate, 2002, 83, 2322-2330.
  24. S. Ravichandran and K. Ramanathan, Molecular interactions with polyacrylamide in ethanolamine, Diethanolamine and Triethanolamine solutions measured ultrasonically, *Polymer-plastics Technology and engineering*, 2008, 47, 169-173.
  25. P. Vasantharani, L. Balu, R. Ezhil Pavai and S. Shailajha, Molecular Interaction Studies on Aniline Containing Organic Liquid Mixtures Using Ultrasonic Technique, *Global Journal of Molecular Sciences* 2009, 4 (1), 42-48.
  26. Ali, A. and Nain, A.K., Ultrasonic studies of formamide + 1,2-ethanediol and sodium iodide + formamide + 1,2-ethanediol mixtures at 298.15 K, *Ind. J. Pure Appl. Phys.*, 1997, 35, 729-733.
  27. Ali, A., Yasmin, A. and Nain, A.K., Study of intermolecular interactions in binary liquid mixtures through ultrasonic speed measurements, *Ind. J. Pure and Appl. Phys.*, 2002, 40, 315-322.
  28. S. Thirumaran and J earnest Jayakumar, Ultrasonic study of n-alkanols in toluene with nitrobenzene, *Ind., J. Pure and Appl. Phys.*, 2009, 47, 265-272.

29. Rita Mehra and Ashish Gupta, Excess parameters of the binary mixtures for benzonitrile + 1-propanol at 298.15, 308.15 and 318.15K, J. Pure and Appl. Ultrason., 2003, 25, 130-135.
30. Ali, A., K. Tiwari, A.K. Nain and V. Chakravorty, Ultrasonic study of molecular interactions in ternary mixtures of dimethyl sulphoxide (1) + carbontetrachloride (2) + aromatic hydrocarbons (3) at 308.15K, Ind. J. Phys., 2000, 74-B (5), 351-355.
31. P. Selvakumari, P. Vasantharani and A.N. Kannappan, Molecular interaction studies in ternary liquid mixture by ultrasonic velocity measurements, J. Curr. Sci. 2006, 9 (1), 95-100.
32. R. Vadamar, P. Mani, R. Balakrishnan and V. Arumugam, Evaluation of excess free volume and internal pressure in binary mixtures of methyl methacrylate with alcohols, E- J. Chem., 2009, 6(1), 261-269.
33. K. C. Basavaraju, T. Damappa, S. K. Rai, Miscibility Studies of Hydroxy Propyl Methyl Cellulose and Poly(ethylene oxide) by Viscometry, Ultrasonic, and Refractometric Methods, Journal of Macromolecular Science, Part B, 2008, 47(3), 417 – 425.
34. Murat Barsbay, Ali Guner, Miscibility of Dextran and Poly (ethylene glycol) in dilute aqueous solutions. II. Effect of Temperature and composition, J. App.Polym.Sci, 2006, 100, 4587-4594.
35. Mima, S., Miya, M., Iwamoto, R. and Yeshikawa, S. Highly deacetylated chitosan and its properties, J. Appl. Polym. Sci., 1983, 28, 1909-1917.
36. Cesteros, I. C., Isasi, J. R. and Issa Katime, Phase Behavior of Poly(4-vinylpyridine)/Poly(vinyl acetate-co-vinyl alcohol) Blends, Macromolecules, 1994, 27(26), 7887-7892.
37. Jean-Jacques Jutier, Even. Lemieux and Robert E. Prud' Homme, Miscibility of polyester/nitrocellulose blends: A DSC and FTIR study, J. Polym. Sci. Part B. Polym. Phys., 2003, 26, 1313-1329.
38. Shia Wei Kuo and Feng Chih Chang, Studies of Miscibility Behaviour and Hydrogen Bonding in Blends of Poly(vinyl phenol) and Poly(vinyl pyrrolidone), Macromolecules, 2001, 34(15), 4089-4097.
39. Silverstein, R. M., Clayton, G., Bassler and Terence, C. Morill, Spectrometric Identification of Organic compounds, John Wiley & Sons Inc., New York, 1991.
40. Ashok kumar gupta, Gautam kumar sah., Miscibility studies of PC/PMMA blends in tetrahydrofuran by viscometry, FTIR and SEM analysis. Nanosystems: Physics, Chemistry, Mathematics, 2013, 4(5), P670-679.



**\*Corresponding Author:**  
[roumana\\_cmi@rediffmail.com](mailto:roumana_cmi@rediffmail.com)