INTERNATIONAL JOURNAL OF SCIENTIFIC PROGRESS AND RESEARCH (IJSPR) ISSN: 2349-4689
Issue 116, Volume 41, Number 01, 2017

Compatibilization of Immiscible Polymer Blends HPMC/PEG using Surfactant Sodium Lauryl Sulphate in Water By Viscosity, Density, Refractive Index and Ultrasonic Velocity Methods

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Abstract: The miscibility of hydroxyl propyl methyl cellulose / Poly (ethylene glycol) (HPMC / PEG) blends with surfactant sodium lauryl sulphate in water has been studied by viscosity, density, refractive index and ultrasonic velocity techniques at laboratory temperature. Using viscosity data, the Chee's differential interaction parameters such as ΔB, μ and Sun's miscibility parameter α were computed. These values revealed that HPMC/PEG blends are immiscible at compositions of 20/80, 40/60, 60/40 & 80/20 with low concentration of sodium lauryl sulphate (0.002%). But the above same blend values were miscible with higher concentration of surfactant sodium lauryl sulphate (0.04%). In addition, the adiabatic compressibility (β_{ad}), intermolecular free length (L_f) and the acoustical impedance (Z) were also calculated.

Key words: Miscibility, REFRACTIVE index, Viscosity, Interaction parameter, surfactants.

I. INTRODUCTION

In seek of new polymeric materials, either new monomers are polymerized nor co-polymerization technique is used to tailor make a new product. An alternative method has been used to blend offered polymer to fabricate materials with desired properties. An apparent advantage of this approach is that usually requires little or no extra capital expenditure comparative to new polymers. The miscibility between the constituents of polymer mixture is an important aspect in the development of new materials based on polymeric blends.[1] Properties of individual synthetic or natural polymers alone are often scarce to produce materials with good chemical, thermal, biological and mechanical performance properties. Blends of synthetic polymers with biological macromolecules have been prepared to obtain polymeric biomaterials2 with special improved properties for certain applications. The blends were produced in diverse forms, like films, sponges or hydrogels and were evaluated as dialysis membranes,[2] wound dressing[3] and drug delivery systems,[4,5] etc. To obtain polymer blends with desired and more useful properties polymer-polymer miscibility is important criteria which may begin from any specific interactions such as hydrogen bonding, dipole –dipole forces and charge transfer complexes between the reliable homo polymers in the blend. There have been a variety of techniques such as SEM, DSC, XRD and FTIR of studying the miscibility of the polymer blends.[6-8] Some of these techniques are complicated, costly and time consuming. Hence it is enviable to identify simple, low cost and rapid techniques also to study the miscibility of polymer blends. Chee[9] and Sun, Wang, and Feng [10] have suggested the viscometric method for the study of polymer – polymer miscibility in solution. Singh and Singh[11-13] have also suggested the use of ultrasonic velocity and viscosity measurements for investigating the polymer miscibility in solution. Palladhi and Singh[14] have shown that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible blends and non- linear for immiscible blends. Recently Chowdoji Rao et al[15-17] used ultrasonic and refractive index techniques to study the miscibility of the polymer blends.

Ultrasonic interferometer is a simple device which yields accurate and reliable data, from which can determine the velocity of ultrasonic sound in a liquid medium. Ultrasonications is used in many applications, such as homogenizing, disintegration, sonochemistry, degassing or cleaning, blow; and find a systematic impression over the various ultrasonic applications and processes. Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. Refractive index is the ratio of the velocity of light in a vacuum to its velocity in a specified medium. Miscibility of polymer-polymer by the method of ultrasonic velocity and density measurements were investigated by Paladhi and Singh.[14-15]

As part of our research work, we have studied the miscibility of HPMC/ PEG blends in water with sodium lauryl sulphate as a surfactant at laboratory temperature by viscosity, ultrasonic velocity, density and refractive index techniques.The main function of a surfactant / compatibilizer in blends is to reduce the surface tension between the two polymers ,and to increase their miscibilities [18]Hydroxy propyl methyl cellulose (HPMC) is a polysaccharide prepared from cellulose. It contains both methyl and hydroxy propyl substitutes. Poly (ethylene glycol) (PEG) is a synthetic water - soluble polymer with good film forming property, which offers good tensile strength (TS), flexibility and barrier properties to oxygen and aroma (SCHELLKENS and Bastiansen, 1991)[19]. PEG is used in all applications of aqueous phase partitioning. For bio-medical separations on the laboratory level, the most commonly used aqueous phase system is composed of Dextron and PEG (Albertson,1986)[20]

II. EXPERIMENTAL

Materials: Hydroxy propyl methyl cellulose - A white powder, solubility of 1% solution in water and colourless, viscosity (2% in water at 25^0 C) 4000 mpa.s. Mfd: Jan-2010, Batch No: 020610, CAS No- 9004-62-0.CENTRAL Drug house (P) Ltd., New Delhi – 110002, (India). Poly (ethylene glycol) 6000 flakes (PEG 6000), $H-(O-CH_2-CH_2)_n-OH$, Average molecular weight 5000-7000, CAS No-25322-68-3,Mfd: Jan-2015, Central Drug house (P) Ltd., New Delhi-110002, (India),and Sodium Lauryl sulphate (Sodium dodecyl sulphate) $C_{12}H_{25}NaSO_4$ (Needle Shape) anionic surfactant. Batch No-60147, Lobha Cheme (P) Ltd. Mumbai-400002.

Preparation of blend solutions: Two kinds of polymers (HPMC and PEG) were discretely dissolved in water for 1% (1g in 100 ml distilled water) w/v) solution. It is worth mentioning that is the preparation of HPMC solution; the HPMC powder must be slowly added to the solvent with gently heating and stirring about one hour at room temperature to obtain a homogeneous solution, otherwise HPMC tends to form sticky clumps when large amounts of samples were added to the solvent. The blends of different composition (20/80, 40/60, 50/50, 60/40 and 80/20) of HPMC/ PEG were prepared of different concentration (0.02%, 0.04%, 0.06%, 0.08% and 0.1%) by stirring the mixtures at room temperature for about 30 minutes. For every concentration of each composition surfactant like sodium lauryl sulphate is to be added. (0.002% and 0.04%).

Preparation of Blend films: The films of the polymers and their blends were prepared by solution casting method. Separate aqueous solution of HMPC and PEG were prepared. A solution of HPMC was added to that of PEG with constant stirring. The mixtures were stirred for one hour by using magnetic stirrer at room temperature to ensure complete mixing with surfactant. Stock solution of HPMC and PEG and their different blend compositions were then casted onto a clean and leveled glass plate and dried using IR lamp in a dust-free chamber. The dried films were peeled off from the glass plate and were found to be transparent. The prepared thin films of pure polymers and their blends were characterized by using FTIR, DSC and SEM analysis methods.

Techniques: Viscosity and density measurements were made at laboratory temperature using Ubbelohde suspended level viscometer (with the flow time of 76 sec for distilled water) and specific gravity bottle, respectively. The required temperature (28°C) was maintained within ± 0.05° C. The ultrasonic velocities of the blend solution with different compositions, namely 0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 0/10 and 100/0 by weight, were measured at 28°C using ultrasonic interferometer. The constant temperature was maintained by circulating water from a thermostat with a thermal stability of ±0.05°C through the double – walled Jacket of ultrasonic experimental cell. The experimental frequency was 2 MHz, and the velocity measurements were accurate to better than 0.05%.The refractive indices of blend solutions with different compositions were measured directly with an Abbes' refracto meter with laboratory temperature 28°C. The accuracy of the refractive index measurement is ± 0.02%.

Fourier Transform Infrared spectroscopy: Fourier transform infrared (FTIR) spectra of HPMC, PEG and their blend films were measured using Perkin Elmer FTIR spectrophotometer to study the nature of molecular interactions. Blend films were characterized at frequencies $650\text{-}4000cm^{-1}$. Dried films were placed vertically in sample holder assembly of the instrument directly and the spectrum was recorded using standard KBr pellet method.

Differential Scanning Calorimeter (DSC) analysis: The DSC analysis was carried out in a calorimeter (DSC Q 200 V24.11 Build 124.) at a heating rate of $10° C\ min^{-1}$ under a nitrogen stream of $10\ ml\ min^{-1}$. For the pure PEG and a mixed blend ratio, the DSC curves was run after the sample has been treated at a desired Tc for 1h. The value of melting point temperature Tm, was estimated from melting peak, by applying the first derivative method. For the pure HPMC and for each HPMC/PEG blend, the equilibrium melting temperature(T_m) was evaluated by using Hoffman-weeks plots,[20] and the miscibility of the system was accessed based on the interaction parameter value (χ_{12}), which was evaluated by applying the Nishi-Wang equation. [21]

X-ray Diffraction: The X-ray diffraction (XRD) pattern of the blend samples were obtained with an intel diffractometer (Paris, France) with monochromatized Cu kα radiation (scan speed of 1 /min in a 2θ range of 5° -4°) at room temperature.

Scanning Electron Microscopic Analysis: The scanning electron microscopic (SEM) micrographs of the blend samples were obtained under high resolution (magnification 150 -300X, 5kV) using JOEL JSM 840 SEM equipped with macromolecules in solution that favors the polymer miscibility. A similar observation was made by Demappa et.al; [22] from their viscometric investigations on intermolecular interactions between hydroxy propyl methyl cellulose /poly ethylene glycol in water.

III. RESULTS AND DISCUSSIONS

Viscosity Studies: The reduced viscosity versus concentration curves for the blends of HPMC/PEG of various compositions in aqueous medium are shown in the figure 1.It has been well established earlier by many workers23,[24] that the disparity of viscosity versus composition plots are linear for miscible and non-linear for immiscible blends. On this basis in the present study, it is noticed that HPMC/PEG blend is found to be miscible only at 50/50 without SLS surfactant, and is immiscible at all the composition at lower concentration(0.02%) of SLS except at 50/50, whereas it is completely miscible at all composition at 0.04% of SLS. The Huggin's plots for reduced viscosity vesus concentration of different HPMC/PEG blend compositions in figure 1 and figure2 respectively. The curves composed of two figures, in figure 1 and the table 1 illustrates that the curves are non-linear and Sun's miscibility parameter was found that the negative value. It may be attributed to that there is no macromolecular interaction in solution (repulsion) hence the polymer blend is immiscible at this composition. In figure 2 and table 1 it indicates that the curves are almost linear and the Sun's miscibility parameter α was fond to be positive is due to the attribution of the mutual attraction of macromolecules in solution which favours the polymer miscibility at all composition at 0.04% SLS.

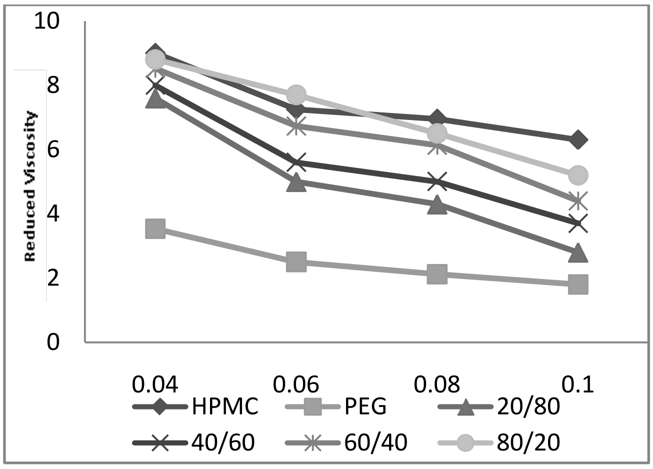


Figure 1. Huggins's plots of hydroxyl prop yl methylcellulose/poly (ethylene glycol) blends with surfactant of sodium lauryl sulphate (0.002%)

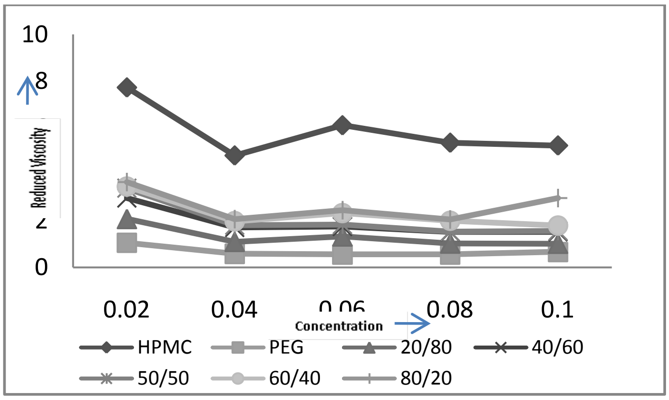


Figure 2. Huggins's plots of hydroxyl propyl methylcellulose/poly (ethylene glycol) blends with surfactant of sodium lauryl sulphate (0.04%)

Chee and Sun Interaction Parameters: To quantify the miscibility of the polymer blends Chee suggested that the general expression for interaction parameter when polymers are mixed in weight fractions w_1 and w_2 is as follows:

The Chee's interaction parameter ΔB, μ (equation 1 and 2) and Sun et al, interaction parameter α (equation 3) shown below with the evidence for the miscibility of polymer blends with surfactant of lower and higher concentrations.(Table 1)

$$\Delta B = \frac{b - b^{-}}{2w_1 w_2} \qquad (1)$$

Where $b^{-} = w_1 b_{11} + w_2 b_{22}$ in which b_{11} and b_{22} are the slopes of the viscosity curves for the pure components. w_1 and w_2 are the weights of the pure polymers.

$b = w_1^2\ b_{11} + w_2^2\ b_{22} + 2w_1, w_2\ b_{12.}$ Where b_{12} is the slope for the blends solution

$$\mu = \frac{\Delta B}{\{[\eta]_1 - [\eta]_2\}^2} \qquad (2)$$

Where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions.

Recently, Sun et al (1992)[10] has suggested a new formula for the determination of polymer miscibility as follows

$$\alpha = K_m - \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2 w_2^2 + 2\sqrt{K_1K_2}[\eta_1][\eta_2]w_1w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \text{ ---------------- } (3)$$

Where, K_1, K_2 and K_m are the Huggin's constants for individual components 1, 2 and the blend respectively. If ΔB, μ and $\alpha > 0$, the blend is miscible, if ΔB, μ and $\alpha < 0$, the blend is immiscible.

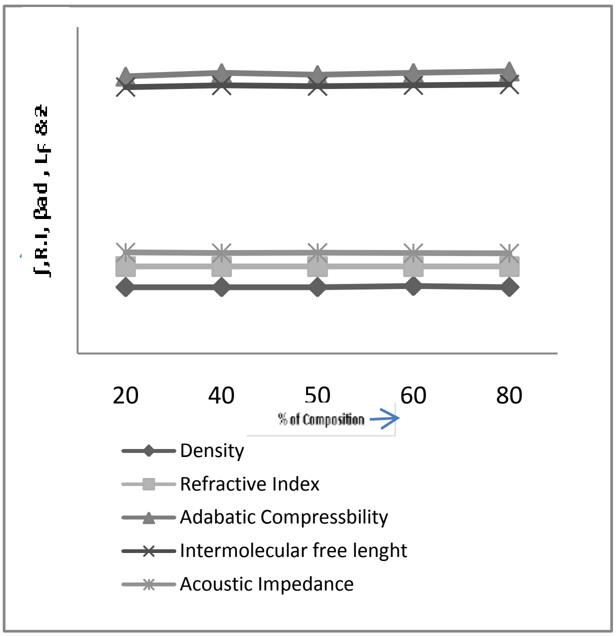


Figure 3. Density, refractive Index, Adiabatic Compressibility, Intermolecular free length & Acoustic Impedance

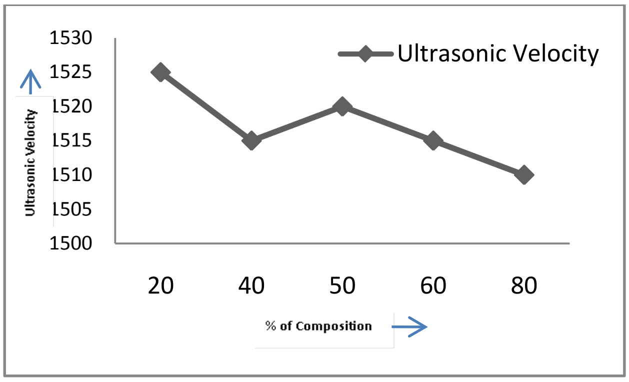


Figure 4. Ultrasonic velocity of HPMC /PEG with surfactant SLS [0.04%]

The adiabatic compressibility $(\beta_{ad})^{22}$ of different blend composition was evaluated using the equation $\beta_{ad} = 1/\rho v^2$ where ρ and v are the density and ultrasonic velocity of composition of blends respectively. The intermolecular free length (L_f) was calculated using the formula $L_f = K\beta^{1/2}$ where $K=1.98\times10^{-6}$, the Jacobson constant the acoustical impendence (Z) was evaluated by using the formula $Z=\rho U$ where 'ρ' is the density of the mixture and 'U' is its ultrasonic velocity.

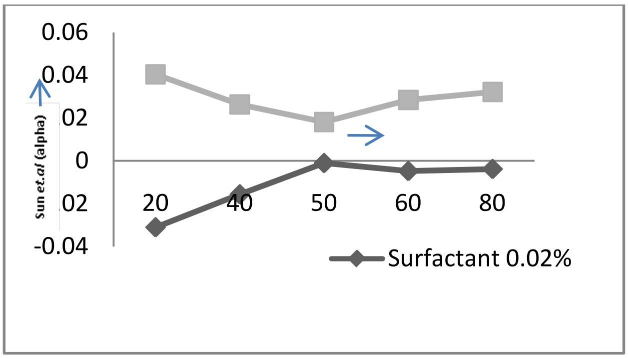


Figure 5. Sun et.al Interaction parameter with surfactant sodium lauryl sulphate [0.02%] and [0.04%]

Fourier Transform Infrared (FTIR) spectral analysis: From FTIR spectra of HPMC, it was found that the peak at 3500 to 3400 cm^{-1} which indicated -OH vibrational stretching in figure 6.[25,26] The symmetric stretching mode of υ_s Me and υ_s hydroxy propyl groups was found at 2900 cm^{-1} in which all the C-H bonds extended and contract in phase.[26]The peak at 2550-2500 cm^{-1} was assigned to -OH stretching vibration, i.e; $\upsilon_{O\text{-}H}$ and intramolecular hydrogen bonding.[25,26]The band between 1650 and 1600 cm^{-1} indicated the presence of stretching vibration of $\upsilon_{c\text{-}o}$ for six membered cyclic rings. Two bending vibrations might occur within a methyl group. Firstly, the symmetric bending vibration of δ_s Me was involved in-phase bending of the C –H bonds. Secondly, the asymmetric bending vibrations of the methoxy group appeared in the region of 1500- 1450 cm^{-1}, the symmetric vibrations were mostly displayed in the range of 1400-1350 cm^{-1}.[27,28]The bond between 1400 and 1350cm^{-1} suggested $\upsilon_{\text{C-O- C}}$ of cyclic anhydrides. The peak at 1300-1250cm^{-1} was due to $\upsilon_{c\text{-}o\text{-}c}$ cyclic epoxide. The band at 1100-1000 $cm^{-1}$was for stretching vibration of ethereal c-o-c groups. The peak at 1000-950 cm^{-1} was due to υ_{as} of pyranose.[29] The rocking mode of CH_2 was found in the range of 850-800 cm^{-1}.

Prominent FTIR peaks of HPMC

3500-3400 Hydroxyl group O-H stretching

vibration, intermolecular

H- bonding

2900 methyl &hydroxy propyl group υ_s-CH stretching

of methyl & propyl

Group

2550-2500 hydroxyl group O-H stretching

		vibration, intramolecular H –bonding
1650-1600	six membered cyclic	υ_{c-o}
1500-1450	δCH, δOCH,δCCH	assymmytric bending vibration of methyl group in CH_3O
1400- 1350	cyclic anhydrides	υ_{c-o-c} and symmetric bending of methoxy group
1300-1250	epoxides	cyclic υ_{c-o-c}
1100-1000	ethereal c-o-c group	stretching vibration of c-o-c group
1000-950	pyranose ring	υ_{as} of pyranose ring
850-800	CH_2 group	rocking mode of CH_2 group

The characteristic band of PEG was observed at 842.41 cm^{-1} due to the c-o-c bending. The blend films that have undergone the step transition show a broader c-o-c band compared with the pure components. This broadening results in a band shift to lower wave number. The change in c-o-c band in the spectrum, suggests that hydrogen bonding is the underlying mechanism in the interaction. In addition, hydrogen bonding has the strongest influence on the donor(in our case the –OH of HPMC) and the absorption maximum of stretching vibration shifts towards lower wave numbers compared to that for the pure HPMC.

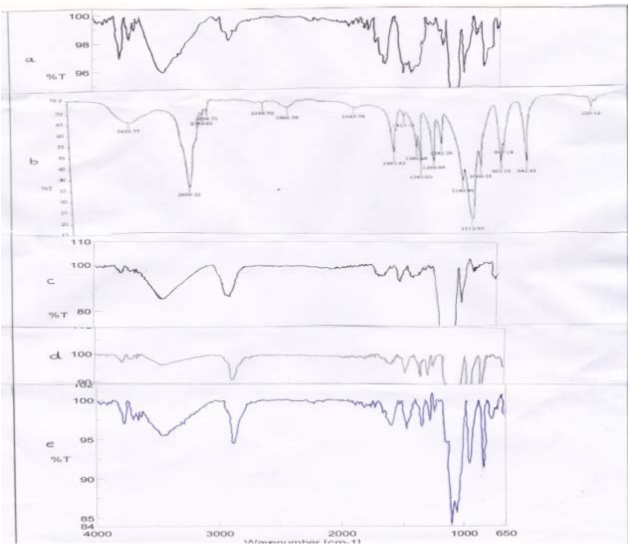


Figure 6. FTIR Spectra of HPMC/PEG and their blends (a) Pure HPMC (b) pure PEG (c) HPMC/PEG 50/50, (d) HPMC/PEG 60/40 and (e) HPMC/PEG 80/20

It is also noticed that the hydroxyl stretching bands became much broader with increasing HPMC content. This strongly supports the idea that a hydrogen bonding can form between ether oxygen atoms of PEG and hydroxy groups of HPMC (scheme 1). This suggests that the HPMC /PEG blends show miscibility when HPMC content is only at 50% without surfactant SLS in the previous publication, the values are in the parenthesis. In this study the blend is immiscible at 0.002% of SLS in all the compositions. But it is found to be completely miscible at 0.04% of surfactant SLS at all the compositions. The immiscible blend is found to be miscible in the presence of sodium lauryl sulphate(0.04%) it may be acts as a surfactant, compatibilizer, and plasticizer.

Differential Scanning Calorimetric studies: We can estimate the polymer – polymer miscibility by determining the glass transition temperature (T_g) of the blend and its composition. Fig (7) shows the DSC curves for pure HPMC (a) and Pure PEG (b) and the HPMC/ PEG blend samples in different compositions 50/50,70/30, and 80/20 (c - e). The difference in the shape and area of thermo grams were noticed. The blends between pure HPMC and Pure PEG will vary the broad area of the polymers. The area became larger and broader with a little sharpness occurred with increase in the content of HPMC in the blends. This variation was attributed to the different degrees of Crystallinity found in the samples with different blend concentrations. The observed change in the area may have indicated the existence of polymer-polymer interaction between HPMC and PEG molecules, through H-bonding between –OH groups of HPMC and – O ⁻ atom of PEG.

It is also clear from the fig (7), that Tg for pure HPMC is observed at 93.7 C° and the Tg of pure PEG is observed at 19- 21C°. We did not expect that two separate transition temperatures would be resolved. If the Tg values of the blended polymer intermediate between those of the parent polymers, this means that it is a miscible polymer blend. Such reports were there in the literature [30, 31] with regard to the miscibility studies of polymer blends by DSC technique. In the present study HPMC/PEG blends show Tg values in between pure compounds that is 56.3 C°, hence the present blend is found to be miscible at all compositions in presence of SLS (0.004%) at laboratory temperature.

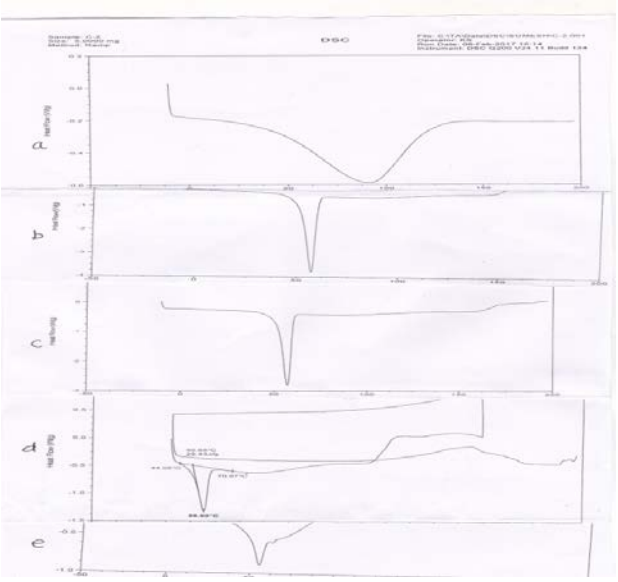


Figure 7. DSC analysis of HPMC /PEG and their blends (a) pure HPMC (b)50/50(c)60/40(d)70/30 and (e) 80/20

X ray diffraction analysis: The measurement of the XRD patterns of polymer blend is also used as a criterion to determine its miscibility. If the two components have low compatibility, then each polymer would have its own crystal region in the blend films, and X-ray patterns of the same would express as simply mixed patterns with the same ratio as those for blending. The typical X-RD patterns of PEG, HPMC and their blend compositions are shown in fig 8. For the pure HPMC (a) there were three peaks around 2θ = 29°, 44.6° and 48°and the intensity peaks 140, 50 and 48 respectively. The diffraction peaks of pure PEG are 2θ= 19.7 -21° and the intensity is found at 45. The blend HPMC/PEG compositions of 70/30 and 80/20 is found to be decreased the intensity with the same 2θ values. The intensity values are shown in figure as 50, 22 and 35 and 68, 22 and 38 in 70/30 and 80/20 respectively. The concentration of HPMC content increases the 2θ values and intensity values of the PEG peaks are found to be decreased and finally at 80/20 the PEG peaks both peaks of 2θ and intensity peaks are disappeared. This indicates that the addition of sodium lauryl sulphate as surfactant, the immiscible polymer blend HPMC/PEG is found to be miscible.

SEM Analysis: Figure 9 represents the SEM images of HPMC (a), PEG and their blends of different compositions such as 50/50(b), 60/40 (c) and 80/20 (d).The surface morphology of pure HPMC is found to be homogeneous. The addition of PEG to HPMC and keeping the concentration of SLS constant (0.004%) there is no phase separation observed in all the compositions. This confirms that the blend HPMC/PEG and the surfactant SLS is found to be miscible in all the compositions at laboratory temperature.

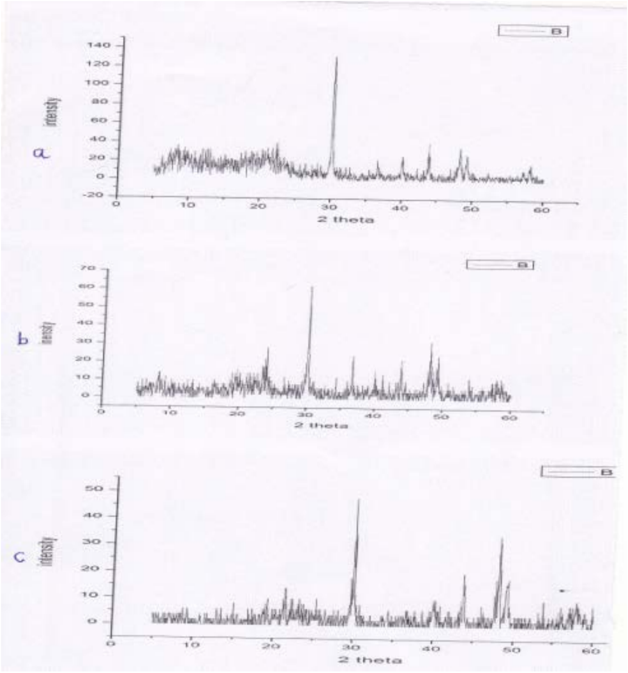
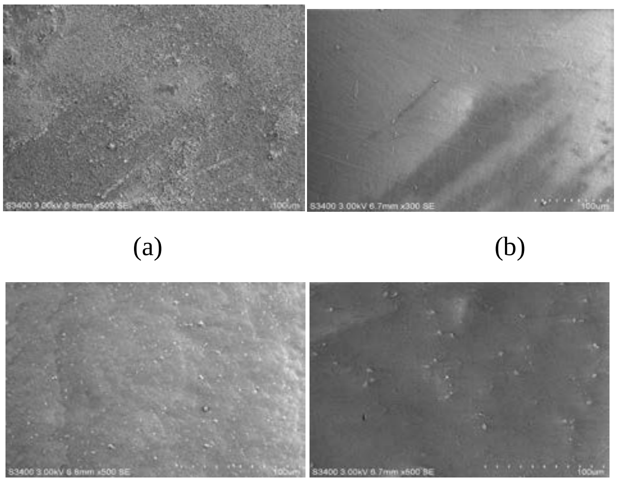


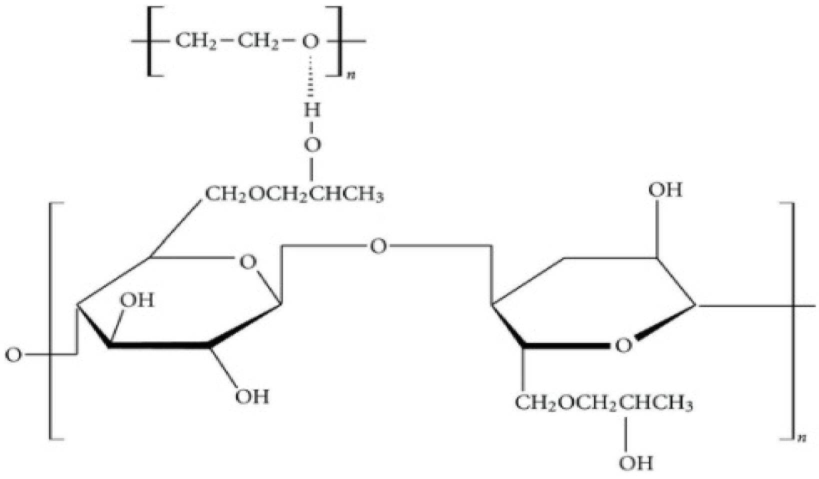
Figure 8. Xray diffraction analysis(a)pure HPMC (b)70/30 (c) 80/20



(a) (b)

(b) (d)

Figure 9. Represents SEM photographs (a) Pure HPMC (b) 50/50 (c) 60/40 (d) 80/20



Scheme1. Hydrogen bond formation between HPMC and PEG

Chee'sdifferential interaction Sun'smiscibility Chee's differential interaction Sun's miscibility
Parameter parameter Parameter parameter

Composition A – HPMC B-PEG A/B	ΔB	μ	α	ΔB	μ	α	β_{ad} x 10^{-10} (Kg/ms^2)	L_f x 10^{-11}	Z x 10^6
	Surfactant 0.002%			Surfactant 0.04%					
20/80	-137.537 (-272.07)	-2.728 (-32.35)	-.031 (-0.340)	-541.25 (-272.07)	-12.057 (-32.35)	+0.0404 (-0.340)	4.244	4.0789	1.545
40/60	-117.00 (-315.20)	-2.321 (-37.47)	-0.0156 (-0.0512)	-456.505 (-315.20)	-10.170 (-37.47)	+0.0264 (-0.0512)	4.298	4.105	1.535
50/50	…….	…..	………	-478.958	-10.669	+0.01818 (+0.0139)	4.270	4.093	1.540
60/40	-143.325 (-429.16)	-2.843 (-51.03)	-0.00475 (-0.0041)	-554.14 (-429.16)	-12.344 (-51.03)	+0.02855 (-0.0041)	4.300	4.106	1.534
80/20	-256.85 (-841.96)	-5.095 (-100.11)	-0.00378 (-0.0022)	-997.55 (-841.96)	-21.776 (-100.11)	+0.0322 (-100.11)	4.324	4.120	1.531

Table 1. Data of ΔB, μ, α, $\beta_{ad,}$ L_f and Z for HPMC / PEG blends with surfactant of different composition.

IV. CONCLUSIONS

The miscibility of HPMS/PEG blends in water in the presence of sodium lauryl sulphate has been studied by solution methods such as viscosity, density, refractive index and ultrasonic velocity techniques at laboratory temperature. The molecular interaction parameters such as ΔB, μ, and α were computed using viscosity data. The prepared films of the HPMC/PEG blends are also characterized for FTIR, DSC, X-RD and SEM to support the data obtained from simple methods such as density, viscosity, refractive index and ultrasonic velocity.

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