

# Hydrogen Bonding Interaction Mediate the Phase Behaviour of an MMA/2-EOEMA Copolymer with P4VPh Blends

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**ABSTRACT:** We have investigated a new type of blend, formed between Methyl Methacrylate-2-Ethoxy Ethyl Methacrylate(MMA/2-EOEMA)Copolymer and with Poly (4-Vinyl Phenol) (P4VPh), that displays unusual phase behaviour. Studies although P4VPh experiences attractive interactions through hydrogen bonding, with both the MMA and 2-EOEMA blocks, its interaction with the former block is significantly stronger. The miscibility and phase behaviour of this novel MMA-2-EOEMA copolymer/P4VPh blend through use of Viscometric, FTIR spectroscopy, DSC thermal analysis and surface morphology studies. The studies were carried out at various blend compositions with N,N Dimethyl Formamide (DMF) as common solvent. From Viscosity data based on sign convention involved in the criterion the values of  $\mu$  and  $\alpha$  for MMA/EOEMA copolymer with P4VPh blends system was computed and found to be positive indicating it is miscible and compatible for all blends composition. The properties of hydrogen bonding interactions of MMA/EOEMA copolymer and P4VPh blends are presented in spectroscopic techniques such as FT-IR studies and the obtained results were further confirmed by DSC thermal analysis and clearly visible from Scanning Electron Microscopy (SEM) images indicated clearly that the morphology of phase separation consists of a matrix of homogeneous mixed MMA-2-EOEMA Copolymer/P4VPh blend. This special phase behaviour and miscibility is due mainly to the diversity of hydrogen bonding interactions.

**KEYWORDS:** MMA/EOEMA copolymer, P4VPh, Blend Compatibility, hydrogen bonding interactions Viscosity, Spectroscopic techniques, DSC thermal analysis, Scanning Electron Microscopy.

## I. INTRODUCTION

The hydrogen bond in polymer blends is an interesting and important subject of research as its presence usually enhances the miscibility of the blend<sup>1</sup>, an attractive way to study intermolecular hydrogen bonding is to combine analysis of experimental crystallographic data with an initio based energy calculations<sup>2</sup> the hydrogen bond analysis is essential for the development of suitable parameters interactions<sup>3</sup>.

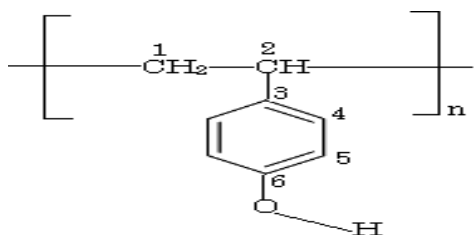
Among miscible polymer blends, hydrogen-bonded systems have played a prominent role there exists a great structural variety of miscible hydrogen-bonding polymer pairs<sup>4-7</sup>. In particular, a considerable amount of literature concerns the miscibility of poly (4-vinylphenol) (P4VPh) with other polymers<sup>8,9</sup>. Poly (4-vinylphenol) is a proton donor that has an easily accessible hydroxyl group of P4VPh and other groups of the partners, such as the carbonyl group in the fourth position of the aromatic ring. It undergoes strong hydrogen-bonding interactions with proton-acceptor polymers such as poly (ethylene oxide)<sup>10</sup>, poly (methyl methacrylate)<sup>11</sup>, and poly (vinyl methyl ketone)<sup>12</sup>. In the past 10 years or so, miscibility of poly(4-vinylphenol) with poly (ether) s<sup>13</sup> and poly (n-alkyl methacrylate) s<sup>14</sup> has been studied using Fourier transform infrared (FT-IR) spectroscopy. On the other hand, the blends have the same fragility as poly (Ethylmethacrylate), which cannot be explained by the energy landscape model. Concentration fluctuations were reduced in the blends as a result of the hydrogen bonding between PEMA and P4VPh<sup>15</sup>. This result implies that the

formation of hydrogen bonds between PVPh and PVP should dominate over that between PVP and PMMA in PMMA-b-PVP/ PVPh blends<sup>16</sup> and MMA-b-EOEMA/P4VPh blends<sup>17</sup>.

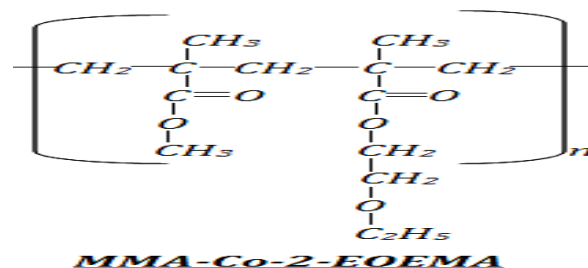
We investigated the interactions and phase behaviours of MMA/EOEMA Copolymer and P4VPh through the use of Viscometric method, Fourier transform infrared (FTIR) spectroscopy, Differential Scanning Calorimetry (DSC) and Scanning Electron Microscopy images indicated the phase separation consists of a matrix of homogeneous mixed MMA-2-EOEMA Copolymer/P4VPh blend. This special phase behaviour and miscibility is due mainly to the diversity of hydrogen bonding interactions.

## II. LITERATURE SURVEY

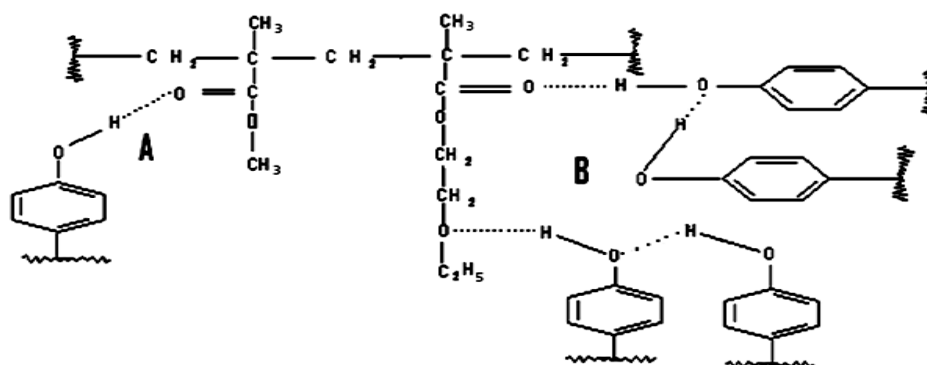
Hydrogen-bonded systems have played a prominent role in miscible and interaction of polymer blends; there exists a great structural variety of miscible hydrogen-bonding polymer pairs. In present study the intermolecular interactions and hydrogen bonding between free hydroxyl groups of P4VPh with ether and ester groups of MMA/2-EOEMA copolymer. P4VPh is a proton donor that has an easily accessible hydroxyl group in the fourth position of the aromatic ring. It undergoes strong hydrogen-bonding interactions with proton-acceptor copolymer shown in the scheme 3.



**Scheme 1** General Structure of PVPh



**Scheme 2** General Structure of MMA/2-EOEMA copolymer



**Scheme 3** Schematic diagram showing possible types of interactions in the blends: (A) Self-association between different P4VPh units; (B) Interassociation between P4VPh and carbonyl or ethoxy group of copolymer.

## III. MATERIALS AND METHODOLOGY

Methyl Methacrylate (MMA), 2-Ethoxy Ethylmethacrylate (EOEMA), poly (4-Vinyl Phenol) (P4VPh), 2, 2-Azo-bis-isobutyronitrile (AIBN) were obtained from Sigma Aldrich chemicals, USA. MMA and 2-EOEMA both monomers were washed with dilute alkali (5% NaOH aq. solution) followed by distilled water and dried over anhydrous CaCl<sub>2</sub> and stored below 0°C. The all other chemicals and solvents used were AR Grade 99 % pure. They are used as received from E-Merck Chemicals, Mumbai, India. The free radical copolymerization of MMA with 2-EOEMA was carried out with 2,2-Azo-bis-isobutyronitrile (AIBN) as an initiator and acetone as solvent. The resulting copolymer was

characterized by FT-IR,  $H^1$ -NMR and  $C^{13}$ -NMR spectroscopic techniques. Formation of MMA/2-EOEMA copolymer is evident by spectroscopic techniques<sup>18</sup>.

### Sample Preparation and Measurement:

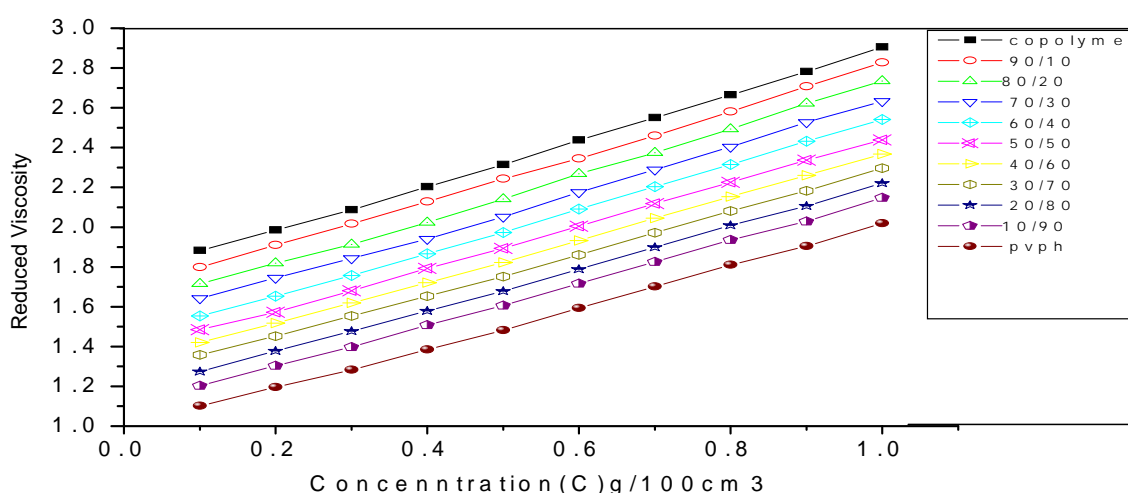
The above synthesized copolymer has been employed in the present study. A dilute polymer solution of 1% w/v was prepared for Viscometric studies. Stock solutions of homo-polymer, Copolymer and the different blend compositions of copolymer and P4VPh were carried out at (A)90/10, (B)80/20, (C)70/30, (D)60/40, (E)50/50, (F)40/60, (G)30/70, (H)20/80, (I)10/90 and P4VPh(w/v %) blend compositions were prepared in Dimethylformamide as a common solvent. Viscosity measurements were made at 30°C using an Ubbelohde Suspended Level Viscometer, during the experiment temperature was maintained by circulating water from a thermostat, with a thermal stability of  $\pm 0.05^\circ\text{C}$ .

For FT-IR, DSC and SEM studies, the thin films of copolymer with P4VPh blends were prepared with neutral solvent DMF. The solution of both polymers at a concentration of 5 percent by weight was cast on Petri dishes at 40°C under  $N_2$  atmosphere. The solvent was allowed to evaporate in a controlled air stream for one day and the resulting films were further dried in vacuum at 50°C for 3-days to ensure total elimination of all the residual solvent. In this way blends were prepared with various compositions range. The films were then peeled off, covered with aluminum foil and kept in the desiccators till further analysis. These films are of the order of microns and transparent.

## III. SIMULATION RESULTS

### Viscometric Studies:

Viscometry is a simple and effective technique for monitoring the interactions and phase behavior in polymer blend solutions. From Viscometric measurements reduced viscosities of pure copolymer and their blends with P4VPh were measured at 30°C, have been calculated and reported. The plot of concentrations against reduced viscosities of copolymers and their blends are shown in Fig 1. The plots are linear no cross over is seen showing that the blends are compatible over all compositions range. The compositions gave higher slope values, indicating strong interactions at those compositions are shown in Table 1



**Fig 1** Reduced viscosities of pure polymers and their blend compositions plotted against concentrations at 30°C

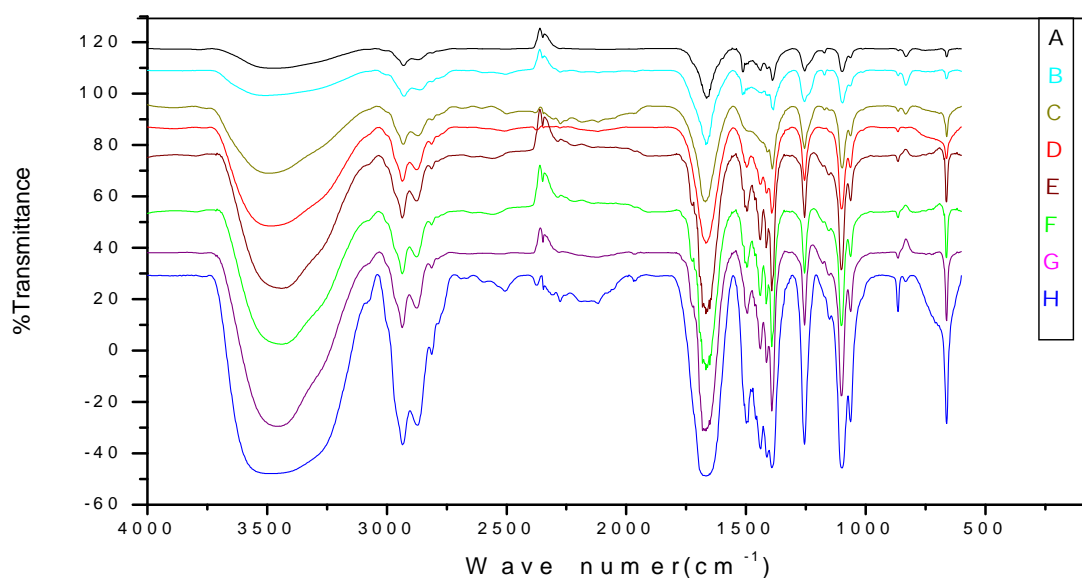
**Table 1** Interaction parameters  $\mu$  and  $\alpha$  of 0.1% w/v, blend of copolymer/ P4VPh at 30°C

% of the Blends	Slope	Wt. of Copoly	Wt. of P4VPh	b	$\bar{b}$	$[\eta]$	$\Delta H$	$\mu$	$\alpha$
<b>Copoly</b>	1.1791	1	0	1.1791	1.1791	1.3648	0	0	0
<b>A</b>	1.2414	0.9	0.1	1.1882	1.1576	1.3473	0.1697	2.4814	0.0257
<b>B</b>	1.1698	0.8	0.2	1.1675	1.1361	1.3204	0.0981	1.4348	0.0099
<b>C</b>	1.1277	0.7	0.3	1.1382	1.1147	1.2928	0.0560	0.8184	0.0986
<b>D</b>	1.1026	0.6	0.4	1.1080	1.0932	1.2644	0.0309	0.4514	0.1156
<b>E</b>	1.0968	0.5	0.5	1.0842	1.0717	1.2352	0.0251	0.3667	0.1424
<b>F</b>	1.1250	0.4	0.6	1.0758	1.0502	1.2143	0.0233	0.3407	0.1894
<b>G</b>	1.0556	0.3	0.7	1.0220	1.0287	1.193	0.0161	0.2360	0.2912
<b>H</b>	1.0428	0.2	0.8	0.9935	1.0073	1.1541	0.124	0.1833	0.2984
<b>I</b>	1.0341	0.1	0.9	0.9786	0.9858	1.1328	0.0096	0.1404	0.3014
<b>PVPh</b>	0.9643	0	1	0.9643	0.9643	1.1033	0	0	0

The polymer blend is miscible if  $\alpha \geq 0$ ,  $\mu \geq 0$  and immiscible when  $\alpha < 0$ ,  $\mu \geq 0$ . In the present study the value of  $\mu$  and  $\alpha$  for copolymer and P4VPh computed to be positive for all the above blends composition predicting the miscibility and compatibility shown in the Table 1.

#### FT-IR Spectroscopy:

FT-IR spectroscopy has been used to identify the specific, intermolecular interactions occurred in copolymer / P4VPh blends. FT-IR analysis confirmed that strong intermolecular hydrogen bonding interactions between the ether groups of the copolymer and the hydroxyl groups of the P4VPh. Schematic representation of the potential favorable intermolecular hydrogen bonding interaction occurred in copolymer / P4VPh blends is shown in the Fig-2



**Fig 2** FT-IR spectra for copolymer /P4VPh blends recorded at room temperature: (A) 10%, (B) 20%, (C) 30%, (D) 40%, (E) 50%, (F) 70%, (G) 80%, (H) 90%

**Table 2** Hydrogen bonding of copolymer with P4VPh blends in different percentage composition

Blend composition of copolymer /P4VPh	Hydrogen bonded		
	Ether group	Carbonyl group	Hydroxyl group
Pure Copolymer	1271.30	1732	-
A	1256.32	1728	2936.13
B	1256.13	1721	2924.63
C	1255.98	1716	2913.24
D	1255.88	1712	2909.89
E	1255.83	1704	2905.15
F	1255.25	1696	2901.14
G	1255.10	1688	2883.28
H	1244.83	1678	2874.53
I	1241.73	1664	2865.79

#### Thermal Analysis:

Thermal analysis were performed on a Universal 4.7A TA Instrument DSC Q200V24.9Bulld121 with a thermal analyst 2000 at a heating rate of 20°C /min. to destroy any thermal history and subsequently quenched into liquid nitrogen. The common method to assess the miscibility of polymer blends is to measure the glass transition temperature of the blend component which represents the onset of the cooperative segmental motion of the component copolymers with P4VPh blends are shown in Table-2 and Fig-3.

The deviations from Fox and Gordon-Taylor equations are to be expected, because of the strong hydrogen bonding between the components, and a least-square fit to the Gordon-Taylor equation gave a value of  $k$  of  $1.2 \pm 0.5$  (95% confidence). The Kwei equation is applicable to polymer blends with specific interactions, such as those which apply in these blends are shown in the Table 4.4.6 and Fig 4.4.8. The nonlinear least-squares "best fit" values obtained for this relationship were  $k = 3.2 \pm 0.8$  and  $q = -144 \pm 42$ , with the relatively large value for  $q$  reflecting the strength of the inter chain hydrogen bonding. Similar values for  $k$  and  $q$  were obtained for comparable blends of P4VPh/ copolymer where  $k = 3.5$  and  $q = -95$ .

**Table 3** Tg Values from: (B) Experimental data; (C) Fox equation; (D) Gordon-Taylor equation;  
(E) Kwei equation

Wt. Fraction of A	Wt. Fraction of B	Result Tg (°C)			
		Exptal Data	FOX	T <sub>G</sub>	K <sub>w</sub>
0	1	33.3	33.3	33.3	33.3
0.1	0.9	38.8	43.4	37.7	29.1
0.2	0.8	36.7	54.1	42.8	27.6
0.3	0.7	38.5	65.6	48.9	28.9
0.4	0.6	44.4	77.9	56.1	33.3
0.5	0.5	54.9	91.2	65.0	41.3
0.6	0.4	70.9	105.5	76.1	53.3
0.7	0.3	93.7	120.9	90.4	70.4
0.8	0.2	125.4	137.7	109.4	94.2
0.9	0.1	169.7	156.0	137.0	127.5
1	0	176	176	176	176

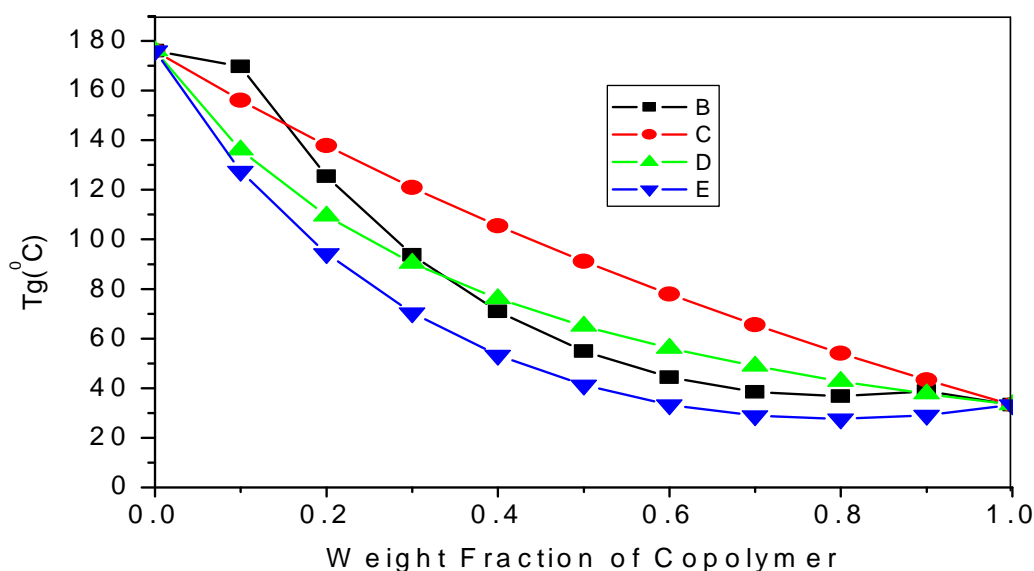


Fig 3 (A) Tg-composition curve: (B) experimental data; (C) Fox equation; (D) Gordon-Taylor equation; (E) Kwei equation

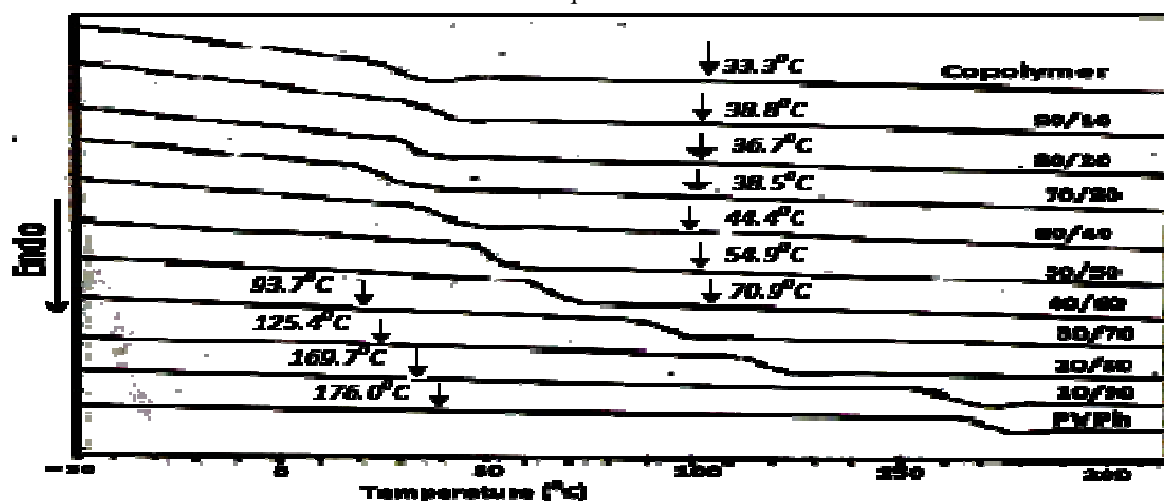


Fig 4 DSC thermograms of copolymer with P4VPh blends

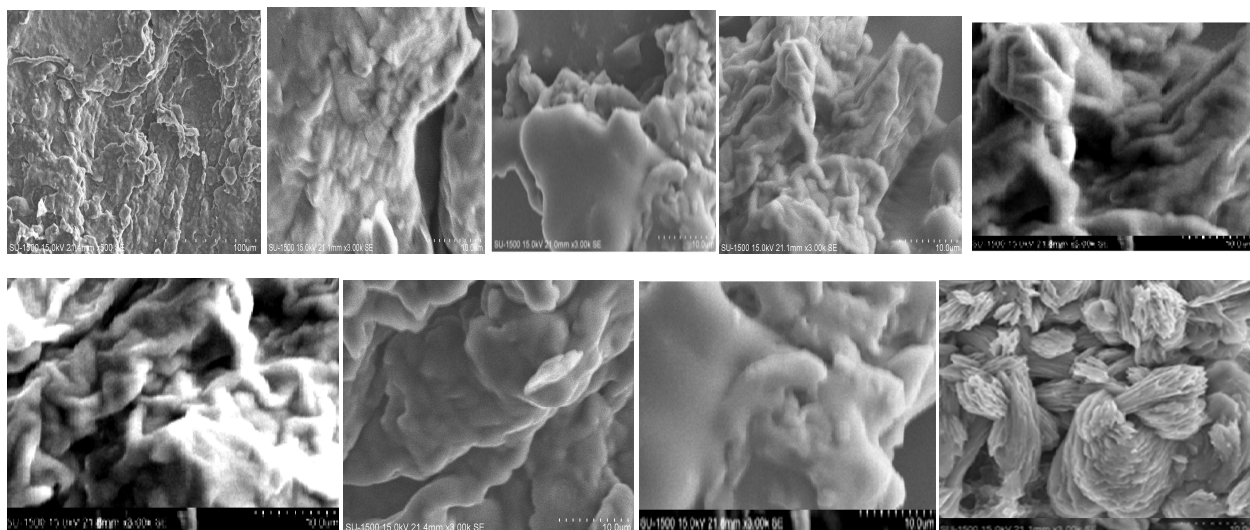
#### Blend Morphology by Scanning Electron Microscope:

In order to confirm phase behavior and morphologies shown by double selective dissolution technique, such as Scanning Electronic Microscopy has been used to characterize all the samples of copolymer with PVPh blends displays SEM micrographs.

The experimentally it has been observed that uniformity of the dispersion was examined through SEM of the solution casting films of copolymer/PVPh blends. It has been observed that when all copolymer concentration the blend showed uniform dispersion (Fig 5). The morphology of copolymer/PVPh revealed that the blends which shows compatibility miscibility and specific interactions in overall percentage of compositions.



# SEM images of copolymer/PVPh blends magnification at 3.00K SE



**Fig 5 Morphology studies of copolymer with PVPh blends at different compositions**

## IV. CONCLUSION

The viscosity, FT-IR and DSC thermal analysis has been used to investigate miscibility, compatibility, hydrogen bonding interactions of the blends. The values calculated from the Viscometric data for  $\mu$  and  $\alpha$  parameter, computed to be positive for all blends composition predicting the miscibility and compatibility for copolymer /P4VPh blends. FT-IR spectroscopy also revealed specific and intermolecular interaction between ester carbonyl and ether groups of copolymer and hydroxyl group of P4VPh is due to hydrogen bonding effect on blends, which shows compatibility miscibility and specific interactions in overall percentage of compositions. A positive deviation of the dependence of  $T_g$  on polymer composition was found based on the Gordon-Taylor and Kwei equation owing to strong hydrogen bonding existing in the copolymer/ P4VPh blends. This was also supported by results from SEM analysis, which probes mixing on a macroscopic level. Even if the structure of copolymer/ P4VPh blends become stiffer and show good mechanical properties in the solid state together with a high swelling ratio, optical clarity and high tacticity have several ideas regarding hydrogen bonds to ketone, ether, ester functional groups, potentially very important for understanding biochemical applications.

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