

# Miscibility, Thermal, and Mechanical Studies of Hydroxypropyl Methylcellulose/Pullulan Blends

P. Prasad,<sup>1</sup> G. S. Guru,<sup>1</sup> H. R. Shivakumar,<sup>1</sup> K. Sheshappa Rai<sup>2</sup>

<sup>1</sup>Department of Chemistry, KVG College of Engineering, Sullia, Karnataka, India

<sup>2</sup>Department of Polymer Science, University of Mysore, Mandya, Karnataka, India

Received 25 July 2007; accepted 2 April 2008

DOI 10.1002/app.28575

Published online 9 July 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Miscibility of blends of hydroxypropyl methylcellulose (HPMC) and Pullulan in common solvent water were studied by viscometry, ultrasonic, density, and refractometric methods at 30 and 40°C. Further the blend films of HPMC and Pullulan were prepared by solution casting method and characterized by Fourier transform IR spectroscopy (FTIR), scanning electron microscopy, tensile measurements, thermogravimetric, and differential scanning calorimetric (DSC) methods. Using the viscosity data, interaction parameters were computed and it suggests that the blend is miscible when the HPMC content is more than 50% in the blend. The change in temper-

ature had no significant effect on the miscibility of HPMC/Pullulan blends. The semimiscibility is confirmed by ultrasonic velocity, density, and refractometric methods. The specific intermolecular interactions of hydrogen bonding type of the blends were investigated by DSC and FTIR. The miscible compositions of HPMC/Pullulan blend showed improved thermal and mechanical properties. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 444–452, 2008

**Key words:** blends; FTIR; miscibility; thermogravimetric analysis (TGA); viscosity

## INTRODUCTION

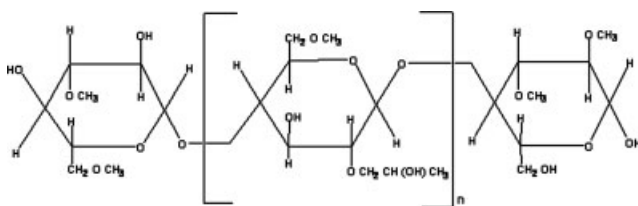
Miscibility of polymers plays an important role in polyblends study and production. The properties of polyblends depend upon the formation of a homogeneous system at a molecular level. At first sight, polymer blends may be classified into homogeneous or miscible, and heterogeneous or immiscible blends.<sup>1,2</sup> Homogeneous blends are relatively rare because the Gibb's free energy of mixing is positive due to the negligible change in entropy, as a consequence of high molecular weight of polymers, and with enthalpy term being positive. The best method of enhancing the miscibility of polyblends is to introduce specific interactions. The potentially useful specific interactions are random dipole, induced dipole, dipole–dipole, hydrogen bonding, acid–base interaction, and charge transfer interactions.<sup>3</sup> Mixing of solutions of interacting polymers produces an immediate precipitate, turbidity, or homogeneity, indicating, respectively, stronger, weaker, and no or very small interaction between the polymers.<sup>4</sup>

Hydroxypropyl methylcellulose (HPMC) is a polysaccharide prepared from cellulose. Chemically, it is a cellulose-ether in which hydroxypropyl groups

have been substituted upon one or more of the three hydroxyl groups present in each anhydroglucose ring of cellulose. HPMC possess characteristic thermal gelling surfactant, nonionic, thickening, film-forming, and adhesive properties coupled, and extremely low toxicity. Films that are heat-sealable, water-soluble, and resistant to oil and greases of animal, vegetable, or mineral origin can be cast from organic solvent systems.<sup>5,6</sup> Pullulan is a natural water-soluble polysaccharide, produced from the fermentation of starch. Pullulan consist of three glucose units linked by  $\alpha$ -1,4-glycosidic linkage as in maltotriose units which are linked by  $\alpha$ -1,6-glycosidic bonds.<sup>7</sup> Both HPMC and Pullulan have many pharmaceutical and biomedical applications.<sup>5–8</sup> The blending of HPMC and Pullulan may enhance their properties and may have better biomedical applications.

In this article, miscibility of HPMC with Pullulan has been thoroughly investigated by a number of techniques. A literature survey reveals the various techniques of studying the miscibility of polymer blends. Chee,<sup>9</sup> Sun et al.,<sup>10</sup> and Jiang and Han<sup>11</sup> have suggested a viscometric method for the study of polymer–polymer miscibility. Das et al.,<sup>12</sup> Paladhi and Singh,<sup>4,13</sup> Varadarajulu et al.,<sup>14</sup> and Rai and coworkers<sup>6,15</sup> showed that the variation of viscosity, ultrasonic velocity, density, and refractive index measurements with blend composition is linear for miscible blends and nonlinear for immiscible blends. Muniz and coworkers<sup>16,17</sup> used the application of

Correspondence to: H. R. Shivakumar (shivakumar17@hotmail.com).



**Scheme 1** Schematic representation of hydroxypropyl-methyl cellulose.

viscometry to check the influence of solvent in blending. The miscibility of polymer blends is directly reflected by scanning electron microscopy (SEM) and Fourier transform IR spectroscopy (FTIR) analysis.<sup>3,18–20</sup>

The thermal properties of polymers are of much importance as a tool in material characterization.<sup>21–24</sup> A detailed understanding of the thermal stability and degradation of polymer is essential for the use of polymeric material in many consumer-oriented applications. Blending polymers has been reported to have much influence on the degradation and thermal properties. Miscibility plays an important role in the degradation and thermal behavior of the blends.<sup>25–30</sup> The studies relating to determination of mechanical properties have been carried out using universal testing machine.

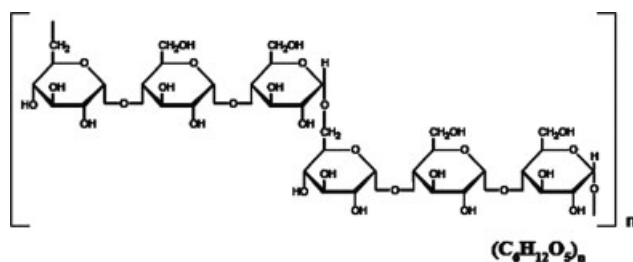
To quantify the miscibility of polymer blends, Chee<sup>9</sup> proposed a general expression to calculate interaction parameter for a ternary system containing two polymers (components 1 and 2) and a solvent (component 3), as

$$\eta_{sp} = [\eta]c + bc^2 \quad (1)$$

$$b = w_1^2 b_{11} + w_2^2 b_{22} + 2w_1 w_2 b_{12} \quad (2)$$

where  $w_1$  and  $w_2$  designates the normalized weight fractions of components 1 and 2, respectively.  $b_{11}$ ,  $b_{22}$ , and  $b_{12}$  are the slopes of the viscosity curves for the components 1 and 2 and the blend, respectively.

Chee considered that the quantity  $b$  reflects the binary interactions between polymer segments and suggested a simple measure of the intermolecular interaction



**Scheme 2** Schematic representation of Pullulan.

$$\Delta B = \frac{b - \bar{b}}{2w_1 w_2} \quad (3)$$

$$\bar{b} = w_1 b_{11} + w_2 b_{22} \quad (4)$$

The interaction parameter  $\Delta B$  is directly proportional to the difference between the observed  $b$  and the average  $\bar{b}$ , which can be determined experimentally. If  $[\eta]_1$  and  $[\eta]_2$  are sufficiently far apart, the factors  $w_1$  and  $w_2$  are expressed in terms of  $[\eta]$ s as

$$\mu = \frac{\Delta b}{\{[\eta]_2 - [\eta]_1\}^2} \quad (5)$$

where  $[\eta]_1$  and  $[\eta]_2$  are intrinsic viscosities of pure component solutions. The polymer blend is miscible if  $\mu \geq 0$  and immiscible when  $\mu < 0$ .

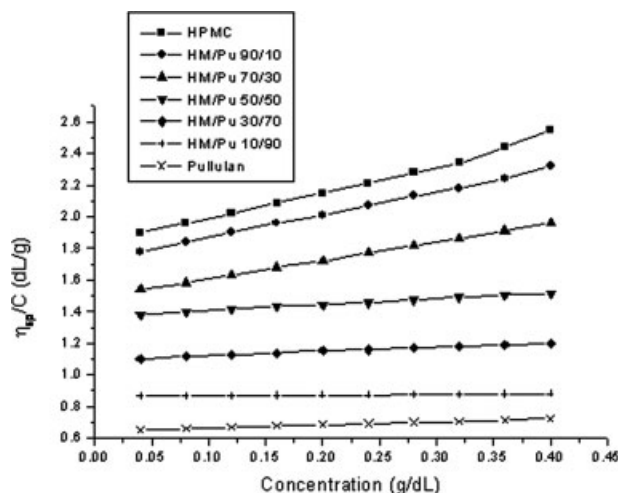
For polymer mixtures, it is found that the intrinsic viscosity of the mixture and those of the components are linearly related by

$$[\eta]_m = [\eta]_1 w_1 + [\eta]_2 w_2 \quad (6)$$

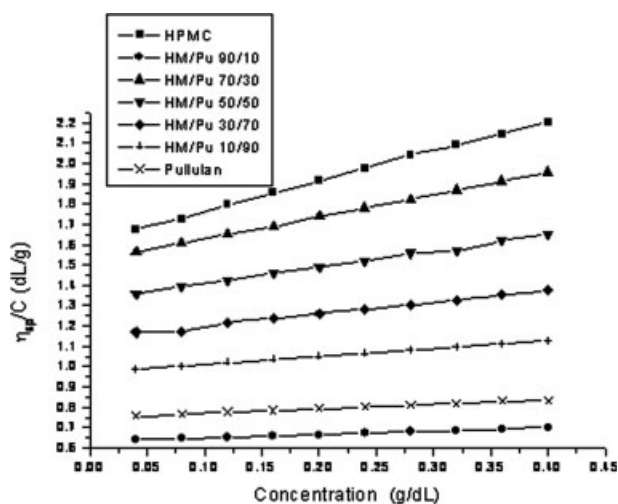
With the above weighed additive rule an expression for Huggin's coefficient  $K_m$  is given as

$$K_m = \frac{K_1 [\eta]_1^2 w_1^2 + K_2 [\eta]_2^2 w_2^2 + 2K_{12} [\eta]_1 [\eta]_2 w_1 w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \quad (7)$$

In the absence of strong specific interaction forces between macromolecules which would encourage aggregation, and at sufficiently low concentration, Sun et al.<sup>10</sup> proposed a new criterion ( $\alpha$ ) for the determination of polymer–polymer miscibility as



**Figure 1** Huggin's plot for 0.4% (w/v) HPMC/Pullulan blends at 30°C.



**Figure 2** Huggin's plot for 0.4% (w/v) HPMC/Pullulan blends at 40°C.

$$\alpha = K_m - \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2 w_2^2 + 2(K_1 K_2)^{1/2} [\eta]_1 [\eta]_2 w_1 w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \quad (8)$$

where  $K_1$  and  $K_2$  are the Huggin's constants for individual components 1 and 2, respectively. The long-range hydrodynamic interactions are considered while deriving the equation. The sign of parameter  $\alpha$  can be used to predict the miscibility of polyblends, when  $\alpha \geq 0$ , miscible;  $\alpha < 0$ , immiscible.

A revised criterion was suggested by Jiang et al.,<sup>11</sup> by replacing parameter  $\alpha$  with  $\beta$ .

$$\beta = \frac{2\Delta K [\eta]_1 [\eta]_2 w_1 w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \quad (9)$$

$$\Delta K = K_{12} - (K_1 K_2)^{1/2} \quad (10)$$

Similarly, when  $\beta \geq 0$ , miscible;  $\beta < 0$ , immiscible. The parameter  $\beta$  is a good criterion for polymer-polymer miscibility determined by viscometry, and

**TABLE I**  
Intrinsic Viscosity and Interaction Parameters of HPMC/Pullulan Blends at 30°C

Blend comp. HPMC/ Pullulan	$[\eta]_{\text{exp}}$ (dL/g)	$[\eta]_{\text{cal}}$ (dL/g)	$\mu$	$\alpha$	$\beta$
100/0	1.840	1.840	—	—	—
90/10	1.721	1.720	0.387	0.0226	0.0532
70/30	1.482	1.481	0.199	0.0671	0.1158
50/50	1.354	1.242	-0.352	-0.2610	-0.0594
30/70	1.100	1.003	-0.439	-0.2633	-0.1286
10/90	0.865	0.764	-0.379	-0.0264	-0.0682
0/100	0.644	0.644	—	—	—

**TABLE II**  
Intrinsic Viscosity and Interaction Parameters of HPMC/Pullulan Blends at 40°C

Blend comp. HPMC/ Pullulan	$[\eta]_{\text{exp}}$ (dL/g)	$[\eta]_{\text{cal}}$ (dL/g)	$\mu$	$\alpha$	$\beta$
100/0	1.616	1.616	—	—	—
90/10	1.524	1.522	0.513	0.0035	0.0664
70/30	1.324	1.322	0.128	0.0014	0.1152
50/50	1.148	1.120	-0.476	-0.1329	-0.0132
30/70	0.972	0.929	-0.439	-0.0455	-0.0327
10/90	0.748	0.733	-0.109	-0.0309	-0.0842
0/100	0.635	0.635	—	—	—

its physical significance is more clear because it is the function of  $[\eta]$ ,  $w$ , and  $\Delta K$ .

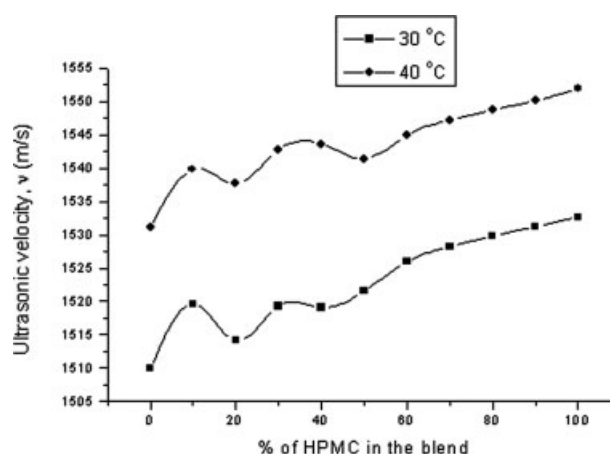
In this study, we have measured the viscosity, ultrasonic velocity, density, and refractive index of different compositions of HPMC/Pullulan blend solutions at 30 and 40°C. Blend films of different compositions of HPMC/Pullulan were prepared by solution casting method and characterized by using FTIR, SEM, tensile measurements, thermogravimetric (TGA), and differential scanning calorimetric (DSC) methods. The  $T_g$  of miscible blend can be predicted using Fox Equation<sup>31</sup> [eq. (11)], Wood's Equation<sup>32</sup> [eq. (12)], or Pochan's Equation<sup>33</sup> [eq. (13)].

$$1/T_g = w_1/T_{g,1} + w_2/T_{g,2} \quad (11)$$

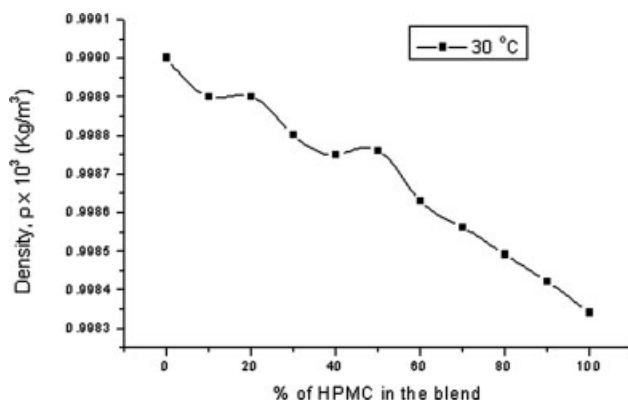
$$T_g = w_1 T_{g,1} + w_2 T_{g,2} \quad (12)$$

$$\ln T_g = w_1 \ln T_{g,1} + w_2 \ln T_{g,2} \quad (13)$$

where  $w_1$  and  $w_2$  designate the normalized weight fractions of components 1 and 2, respectively.  $T_{g,1}$  and  $T_{g,2}$  are the glass transition temperatures for the components 1 and 2, respectively.



**Figure 3** Effect of temperature on the variation of ultrasonic velocity with the composition of 1% (w/v) of HPMC/Pullulan at 30 and 40°C.

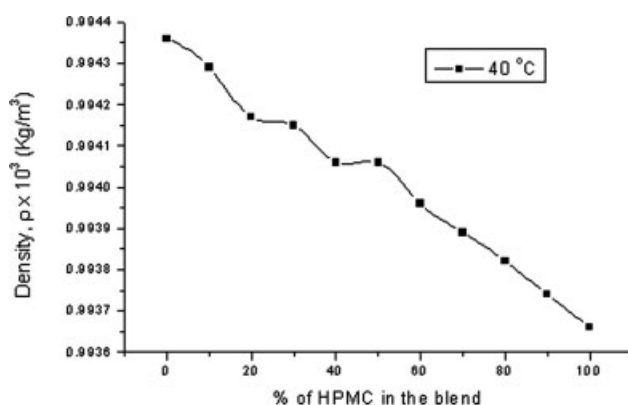


**Figure 4** Effect of temperature on the variation of density with the composition of 1% (w/v) of HPMC/Pullulan at 30°C.

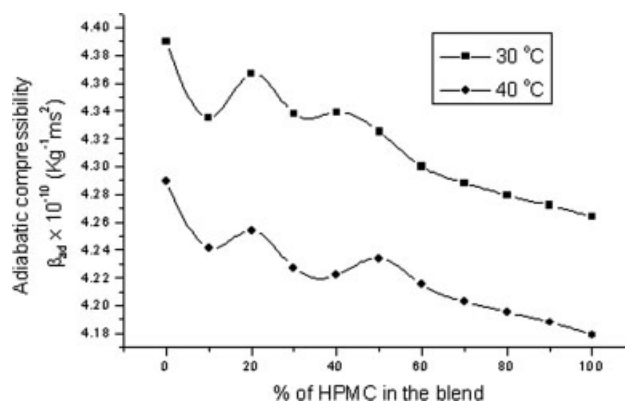
### EXPERIMENTAL

Blends of HPMC/Pullulan of different compositions were prepared by mixing aqueous polymer solutions. The polymers employed in this study are HPMC (Rolex, India;  $M_w \approx 60,000$ ) and Pullulan [Nutriscience Innovations LLC, Fairfield, CT;  $M_w$  100 cst (10 wt %, 30°C)]. The structure of HPMC and Pullulan are shown in Schemes 1 and 2, respectively.

Stock solutions of HPMC and Pullulan were prepared (0.4%, w/v). The blend stock solutions (90/10, 70/30, 50/50, 30/70, and 10/90) were prepared by stirring the mixtures at room temperature for about 45 min. Using the above pure and blend stock solutions, different blend solutions [0.04, 0.08, 0.12, 0.16, 0.20, 0.24, 0.28, 0.32, 0.36, and 0.4 (w/v) concentrations] were prepared and viscosity measurements were done at 30 and 40°C using an Ubbelohde suspended level viscometer. Different temperatures were maintained using a thermostat bath with a thermal stability of  $\pm 0.05^\circ\text{C}$ .



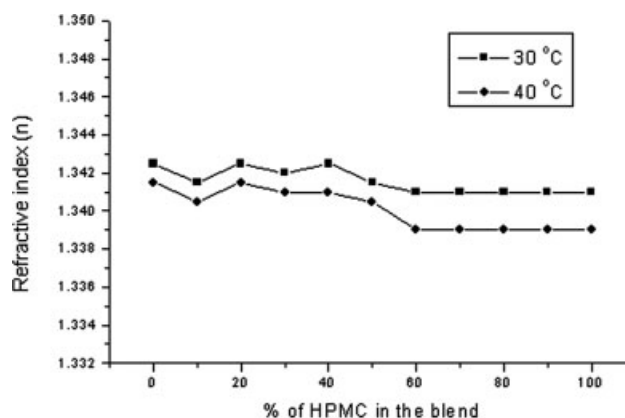
**Figure 5** Effect of temperature on the variation of density with the composition of 1% (w/v) of HPMC/Pullulan at 40°C.



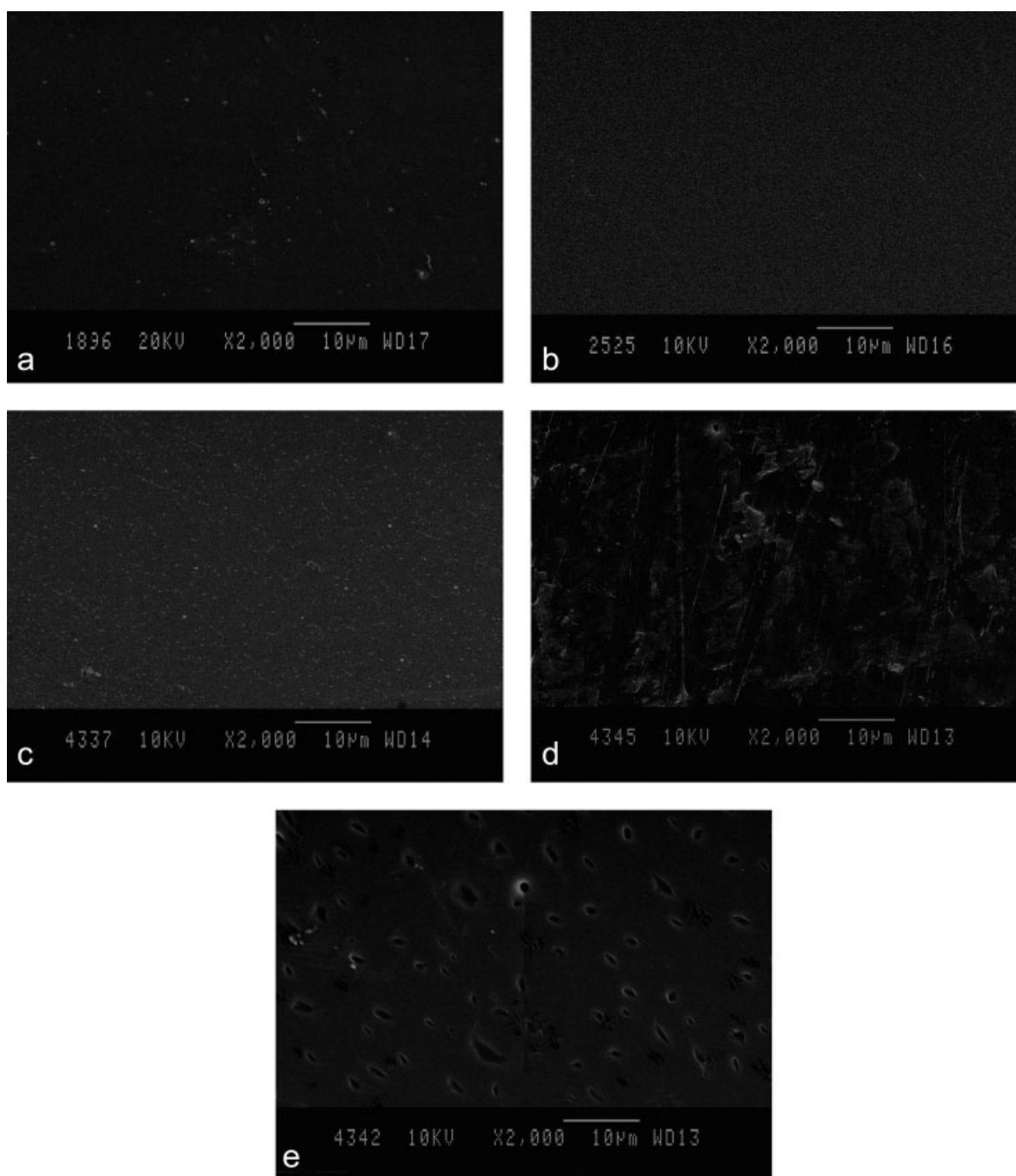
**Figure 6** Effect of temperature on the variation of adiabatic compressibility with the composition of 1% (w/v) of HPMC/Pullulan at 30 and 40°C.

Ultrasonic velocity of the blend solutions of 1% (w/v) were measured at 30 and 40°C by an interferometric technique<sup>6,12-15</sup> employing an ultrasonic interferometer (Mital Enterprises, New Delhi, India) at a frequency of 2 MHz. The densities and refractive index of the HPMC/Pullulan blend solutions (1%, w/v) were measured at 30 and 40°C using specific gravity bottle and refractometer, respectively.

Thin films of the polymers and their blends were prepared by solution casting method. Separate aqueous solutions of HPMC and Pullulan were prepared. A solution of Pullulan was added to that of HPMC with constant stirring. The mixture was stirred for 45 min at room temperature to ensure complete mixing. The total polymer concentration was kept at 1% (w/v). Stock solutions of HPMC and Pullulan and their different blend compositions were then casted onto a Teflon-coated clean glass plate and dried using IR lamp in a dust free atmosphere. The dried thin films were peeled off from the glass plate and were found to be transparent.



**Figure 7** Effect of temperature on the variation of refractive index with the composition of 1% (w/v) of HPMC/Pullulan at 30 and 40°C.



**Figure 8** Scanning electron micrographs for (a) Pure HPMC, (b) Pure Pullulan, (c) 70/30 HPMC/Pullulan blend, (d) 50/50 HPMC/Pullulan blend, and (e) 30/70 HPMC/Pullulan blend.

FTIR spectroscopy<sup>3,19</sup> was used to detect hydrogen bonding interaction between HPMC and Pullulan in their blends. FTIR spectra were measured using NICOLET AVATAR 530 spectrophotometer. Scanning electron microscopic analysis<sup>18,20</sup> were recorded using a JOEL (JSM 6380LA) analyzer.

TGA analysis<sup>21–24</sup> of the blend films were performed over temperature range of 20–500°C, using TGA analyzer (TGA Q50 V20.2 Build 27) under nitrogen environment at a scan rate of 10°C/min.

DSC<sup>25–30</sup> thermograms were produced with a TA Q200 differential scanning calorimeter, under nitrogen environment. The first temperature cycle heated the sample to 90°C, where it remained isothermal for between 15 and 60 min to remove the remaining water in the samples. The sample was then cooled to 20°C before it was immediately reheated to 250°C. The heating/cooling rate was set at 10°C/min.

Mechanical properties<sup>28–30</sup> of blend films were measured under tensile strain. Five samples (10 ×

150 mm<sup>2</sup>) for each film were tested for mechanical properties. Before testing, all the samples were conditioned for 2 days. Thicknesses of the samples measured with a micrometer having a sensitivity of 1  $\mu$ m are found to be 0.08 mm. Tensile strength at yield (TS), tensile modulus, and percentage of elongation at break (*E*) were determined with an LLYODS UK model analyzer (LR 100K) according to ASTM D 882; the test was run at 100 mm/min and at room temperature.

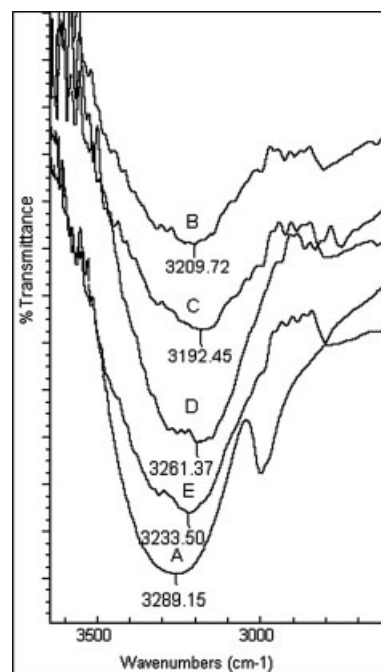
## RESULTS AND DISCUSSION

### Solution studies

Reduced viscosities of homopolymers HPMC, Pullulan, and their blend compositions (90/10, 70/30, 50/50, 30/70, and 10/90) were measured at 30 and 40°C. Huggin's plots of reduced viscosities of the pure polymers and their blend compositions against concentrations are shown in Figures 1 and 2, respectively; the plots were linear. A higher slope variation for 90/10 and 70/30 compositions may be attributed to the mutual attraction of macromolecules in solution which leads to the increase of hydrodynamic volume. Below this critical concentration, a sharp decrease in the slope is observed because of phase separation.<sup>15,14,34</sup>

The intercept of reduced viscosity versus concentration plots gives the intrinsic viscosity of the corresponding polymer and their blend, which are presented in Tables I and II, respectively. The experimental intrinsic viscosity values thus obtained are compared with their weighed average values. The experimental values were found to be slightly higher than the theoretical values for 90/10 and 70/30 compositions at both temperatures indicating miscibility, whereas a large deviation is observed for 50/50, 30/70, and 10/90 compositions indicating immiscibility.<sup>6,14,15</sup> Computed values of interaction parameters  $\mu$ ,  $\alpha$ , and  $\beta$  based on Chee, Sun et al., and Jiang and Han approaches were found to be positive for 90/10, 70/30 compositions at 30 and 40°C and negative for 50/50, 30/70, and 10/90 compositions. Hence, HPMC/Pullulan blend is miscible when HPMC content is more than 50% in the blend. The values of interaction parameters  $\mu$  (Chee's),  $\alpha$  (Sun et al.'s), and  $\beta$  (Jiang and Han's) indicate that the change in temperature had no significant effect on the miscibility of HPMC/Pullulan blends (Tables I and II).

To confirm the miscibility or otherwise of these blends, separate plots of the variation of ultrasonic velocity ( $v$ ), density ( $\rho$ ), adiabatic compressibility ( $\beta_{ad}$ ), and refractive index ( $n$ ) versus composition were plotted over an extended range of concentrations of the blend solutions at 30 and 40°C (Figs. 3–7, respectively). Plots were almost linear for higher



**Figure 9** FTIR spectra of (A) Pure Pullulan, (B) Pure HPMC, (C) 70/30 HPMC/Pullulan blend, (D) 50/50 HPMC/Pullulan blend, and (E) 30/70 HPMC/Pullulan blend.

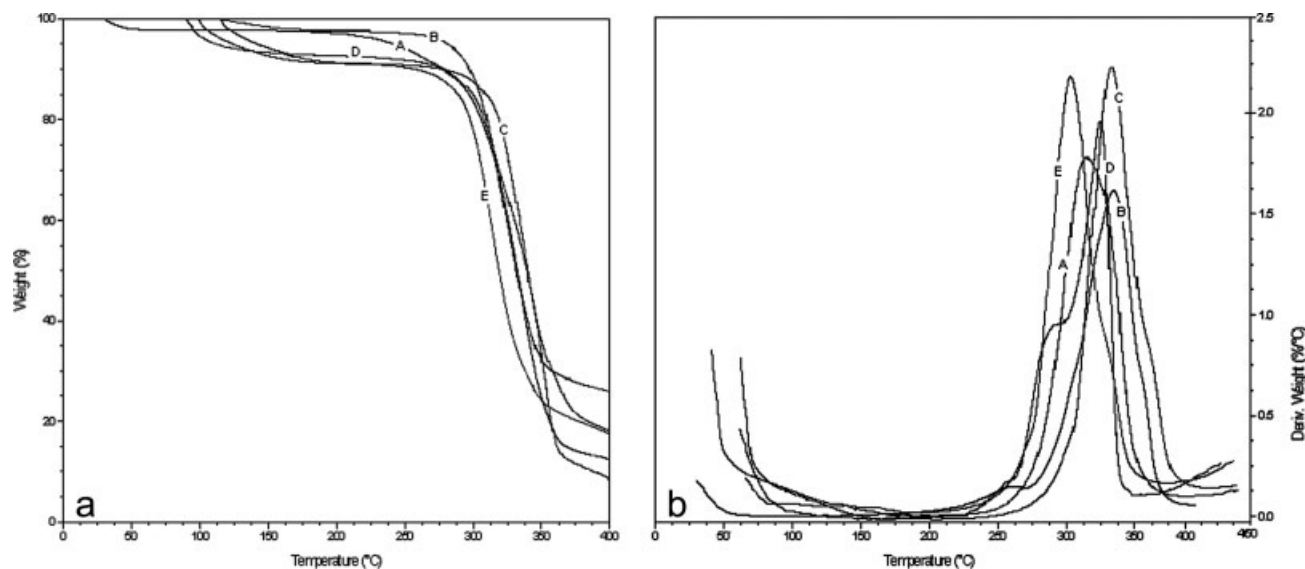
proportions of HPMC confirming miscibility<sup>6,14,15</sup> and lower proportions deviated from linearity indicating phase separation (immiscibility). The behavior indicates that HPMC/Pullulan blend is semimiscible in aqueous solutions.

### Morphology study of HPMC/Pullulan blends

Uniformity of the dispersion was examined through SEM of the solution-casted films of 100/0, 70/30, 50/50, 30/70, and 0/100 HPMC/Pullulan blends. Results indicated that there was phase separation for 50/50 and 30/70 compositions [Fig. 8(d,e)], whereas 70/30 blend shows homogeneity [Fig. 8(c)]. The morphology of HPMC/Pullulan reveals that the blend is semimiscible.

### FTIR spectroscopic study

FTIR spectra of pure HPMC, Pullulan, and their blend films (100/0, 70/30, 50/50, 30/70, and 0/100) were recorded. The spectral data reveal the miscibility at 70/30 blend composition. Figure 9 shows the comparison of —OH frequency of pure Pullulan (A), pure HPMC (B), and 70/30 blend composition (C). The —OH stretching of the hydroxyl group appeared at 3209 cm<sup>-1</sup> for pure HPMC and 3289.15 cm<sup>-1</sup> for pure Pullulan. For the 70/30 blend composition, this peak appeared at 3192.45 cm<sup>-1</sup>. The result confirms the formation of intermolecular hydrogen bonding.



**Figure 10** (a) TGA curves of (A) Pure Pullulan, (B) Pure HPMC, (C) 70/30 HPMC/Pullulan blend, (D) 50/50 HPMC/Pullulan blend, and (E) 30/70 HPMC/Pullulan blend. (b) Derivative (TGA) curves of (A) Pure Pullulan, (B) Pure HPMC, (C) 70/30 HPMC/Pullulan blend, (D) 50/50 HPMC/Pullulan blend, and (E) 30/70 HPMC/Pullulan blend.

Similar observations were reported by Toti et al.<sup>19</sup> for blend membranes of sodium alginate and poly(acrylamide)-*graft*-gaur gum.

### TGA study

The blend samples were made in different compositions such as 70/30, 50/50, and 30/70 of HPMC and Pullulan, and TGA analysis was performed using TGA analyzer under nitrogen environment. The TG curves and its derivative are given in Figure 10(a,b). To determine the thermal stability trend, the temperature characteristics such as  $T_0$  (temperature of onset of decomposition),  $T_{20}$  (temperature for 20% mass loss),  $T_{40}$  (temperature for 40% mass loss),  $T_{50}$  (temperature for 50% mass loss),  $T_{60}$  (temperature for 60% mass loss), and  $T_{max}$  (temperature for maximum mass loss) were calculated and presented in Table III.

$T_0$ ,  $T_{20}$ ,  $T_{40}$ ,  $T_{50}$ ,  $T_{60}$ , and  $T_{max}$  are the main criteria of the thermal stability of blends and signal features of the TG curves. A comparison of the decomposition temperature values of HPMC/Pullulan blend series shows that 30/70 blends possess the lowest value, and it is increased in 50/50 and shows highest value for 70/30 blends. The thermal stability of blend compositions increases with increase in percentage composition of HPMC in the blend, and 70/30 blends have higher thermal stability.

### Glass transition and miscibility

The thermal properties of HPMC, 70/30 HPMC/Pullulan blends, and Pullulan were studied by means of DSC- $T_g$  determinations and the thermograms are

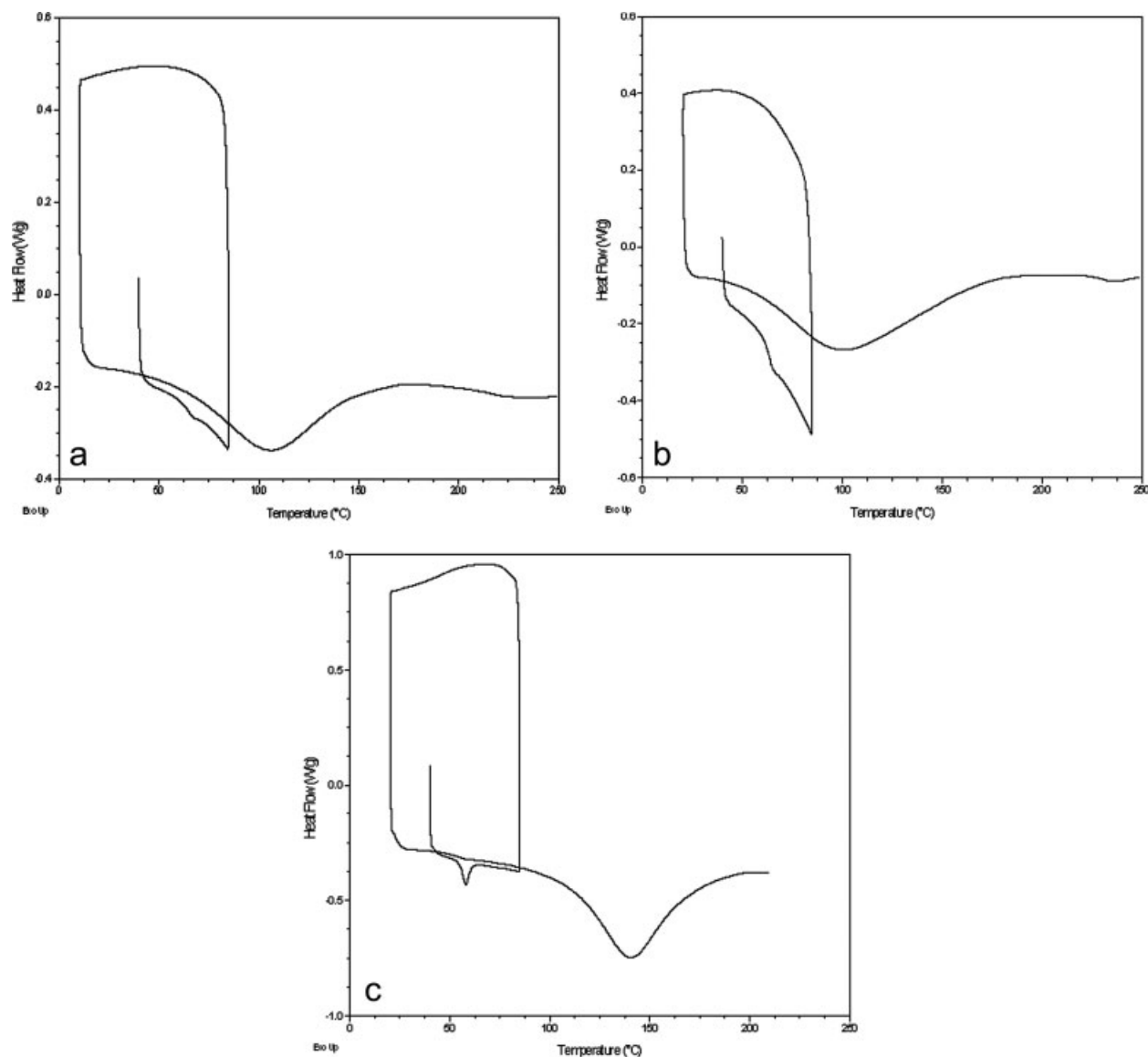
given in Figure 11. As it is observed in the respective traces, the 70/30 HPMC/Pullulan blend showed single composition-dependent glass transition temperature  $T_g$  between the  $T_g$  of the pure HPMC and that of the pure Pullulan, indicating miscibility. The glass transition temperature was taken as the mid-point of the change of slope in the DSC curves.<sup>26</sup> The melting temperatures of HPMC, 70/30 HPMC/Pullulan blends, and Pullulan, and experimental  $T_g$  value for 70/30 HPMC/Pullulan blend compared with theoretical  $T_g$  values<sup>28</sup> are summarized in Table IV. Experimental  $T_g$  value for 70/30 HPMC/Pullulan blends is found to be slightly higher than that of theoretically calculated  $T_g$  value indicating an intermolecular interaction between the polymers.<sup>34</sup>

### Mechanical property studies

The TS, % elongation, and tensile modulus ( $E$ ) of pure HPMC, Pullulan, and their blend films (100/0, 90/10, 70/30, 50/50, 30/70, 10/90, and 0/100) were measured and shown in Table V. The TS, % elonga-

**TABLE III**  
Parameters Evaluated From the Thermograms and Thermoderivatograms of HPMC/Pullulan Blends

Blend comp. HPMC/Pull	Temperature at different weight loss ( $\pm 0.5^\circ\text{C}$ )					
	$T_0$	$T_{20}$	$T_{40}$	$T_{50}$	$T_{60}$	$T_{max}$
100/0	178	306	325	333	341	352
70/30	225	288	323	333	338	355
50/50	213	284	313	326	333	347
30/70	191	283	301	308	320	344
0/100	209	272	289	309	313	322



**Figure 11** DSC traces of (a) Pure HPMC, (b) 70/30 HPMC/Pullulan blend, and (c) Pure Pullulan.

tion, and tensile modulus were found to be  $\sim 36$  MPa, 16%, 619 MPa, and 36 MPa, 4%, 988 MPa for pure HPMC and pure Pullulan, respectively. The observed values are smaller for 10/90, 30/70, and 50/50 HPMC/Pullulan blend compositions, which may be due to lack of interaction between the components of the blends. Mechanical properties of

blend compositions were increased with increase in percentage composition of HPMC in the blend above 50% of HPMC content in the HPMC/Pullulan blends due to strong intermolecular interactions. 90/10 HPMC/Pullulan blends showed improved yield strength and tensile modulus (41.42 and 1045.7 MPa) than pure HPMC and pure Pullulan.

**TABLE IV**  
Melting Temperature ( $T_m$ ), Experimental, and Theoretical Glass Transition Temperature ( $T_g$ ) of HPMC, Pullulan, and HPMC/Pull 70/30 Blend

Blend comp. HPMC/Pull	Melting temperature $T_m$ ( $^{\circ}\text{C}$ )	Experimental $T_g$ values ( $^{\circ}\text{C}$ )	Theoretical $T_g$ values ( $^{\circ}\text{C}$ )		
			Fox equation	Wood equation	Pochan's equation
100/0	106.25	65.63	–	–	–
70/30	96.88	63.28	62.21	62.58	62.39
0/100	140.63	55.47	–	–	–



**TABLE V**  
**Parameters Obtained From the Mechanical Property**  
**Studies of HPMC/Pullulan Blends**

Blend comp. HPMC/Pull	Tensile strength at yield (MPa)	% Elongation	Tensile modulus (MPa)
100/0	35.51	15.75	619.1
90/10	41.42	5.55	1045.7
70/30	30.77	5.18	704.3
50/50	10.52	2.35	487.6
30/70	13.39	3.08	528.4
10/90	19.06	2.48	510.9
0/100	36.20	4.37	987.5

### CONCLUSIONS

Based on viscosity, ultrasonic velocity, density, and refractive index measurements, it is found that the polymer blend of HPMC/Pullulan is miscible when the HPMC content is more than 50%. Below this critical HPMC concentration, the blends were found to be immiscible. Hence HPMC/Pullulan blend in aqueous solution at 30 and 40°C is semimiscible in nature. Variation of temperature did not have any significant effect on the miscibility. Homogeneity of miscible compositions of HPMC/Pullulan blends and specific intermolecular interactions of hydrogen bonding type were investigated, and semimiscibility of the blends was confirmed. The thermal and mechanical properties improved in miscible compositions of HPMC/Pullulan blends.

The authors gratefully acknowledge Dr. Kurunji Venkataramana Gowda (Founder President, AOLE, Sullia), Dr. S. G. Gopalakrishna (Principal, KVG College of Engineering, Sullia), and Dr. A. N. Shetty (NITK, Surathkal), for providing infrastructure facility.

### References

1. Utraki, L. A. *Polymer Alloys and Blends*, Vol. 3; Hanser Publications: New York, 1989.
2. Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic Press: New York, 1979.

3. Liu, C.; Xiao, C.; Liang, H. *J Appl Polym Sci* 2005, 95, 1405.
4. Paladhi, R.; Singh, R. P. *Eur Polym J* 1994, 30, 251.
5. SBP. *Handbook of Industrial Gums and Resins*; SBP Board of consultants and Engineers: New Delhi, 1998.
6. Jayaraju, J.; Raviprakash, S. D.; Keshavayya, J.; Rai, S. K. *J Appl Polym Sci* 2006, 102, 2738.
7. Leathers, T. D. In *Polysaccharides and Polyamides in the Food Industry: Properties, Production, and Patents*, Vol. 1: Polysaccharides; Steinbuchel, A., Rhee, S. K., Eds.; Wiley-VCH: Weinheim, 2005; Chapter 11.
8. Zeng, M.; Fang, Z.; Xu, C. *J Appl Polym Sci* 2004, 91, 2840.
9. Chee, K. K. *Eur Polym J* 1990, 26, 423.
10. Sun, Z.; Wang, W.; Feng, Z. *Eur Polym J* 1992, 28, 1259.
11. Jiang, W. H.; Han, S. J. *Eur Polym J* 1998, 34, 1579.
12. Das, S.; Singh, R. P.; Maiti, S. *Polym Bull* 1980, 2, 403.
13. Paladhi, R.; Singh, R. P. *J Appl Polym Sci* 1994, 51, 1559.
14. Varadarajulu, A.; Reddy, R. L.; Siddaramaiah. *J Appl Polym Sci* 1998, 70, 1823.
15. Raviprakash, S. D.; Rai, S. K. *J Polym Mater* 2005, 22, 189.
16. Crispim, E. G.; Rubira, A. F.; Muniz, E. C. *Polymer* 1999, 40, 5129.
17. Crispim, E. G.; Schuquel, I. T. A.; Rubira, A. F.; Muniz, E. C. *Polymer* 2000, 40, 933.
18. Peesan, M.; Supaphol, P. *Carbohydr Polym* 2005, 60, 343.
19. Toti, U. S.; Aminabhavi, T. M. *J Appl Polym Sci* 2002, 85, 2014.
20. Thakore, M.; Sonal, D.; Sarwade, B. D.; Devi, S. *J Appl Polym Sci* 1999, 71, 1851.
21. Nair, M. N. R.; Thomas, G. V.; Nair, M. R. G. *Polym Degrad Stab* 2007, 92, 189.
22. Canetti, M.; Bertini, F.; De Chirico, A.; Audisio, G. *Polym Degrad Stab* 2006, 91, 494.
23. Guo, Z.; Fang, Z.; Tong, L.; Xu, Z. *Polym Degrad Stab* 2007, 92, 545.
24. Santra, R. N.; Mukunda, P. G.; Nando, G. B.; Chaki, T. K. *Thermochim Acta* 1993, 219, 283.
25. Papageorgiou, G. Z.; Bikiaris, D. N. *J Polym Sci Part B: Polym Phys* 2006, 44, 584.
26. Lai, W.-C.; Liau, W.-B. *J Appl Polym Sci* 2004, 92, 1562.
27. Kweon, D.-K.; Kawasaki, N.; Nakayama, A.; Aiba, S. *J Appl Polym Sci* 2004, 92, 1716.
28. Linares, A.; Acosta, J. L. *J Appl Polym Sci* 2004, 92, 3030.
29. Agari, Y.; Sakai, K.; Kano, Y.; Nomura, R. *J Polym Sci Part B: Polym Phys* 2007, 45, 2972.
30. Su, J.-F.; Huang, Z.; Liu, K.; Fu, L.-L.; Liu, H.-R. *Polym Bull* 2007, 58, 913.
31. Fox, T. G. *Bull Am Phys Soc* 1956, 1, 123.
32. Wood, L. A. *J Appl Polym Sci* 1991, 29, 649.
33. Pochan, J. M.; Beatty, C. L. Pochan, D. F. *Polymer* 1979, 20, 879.
34. Rao, V.; Ashokan, P. V.; Shridhar, M. H. *Polymer* 1999, 40, 7167.