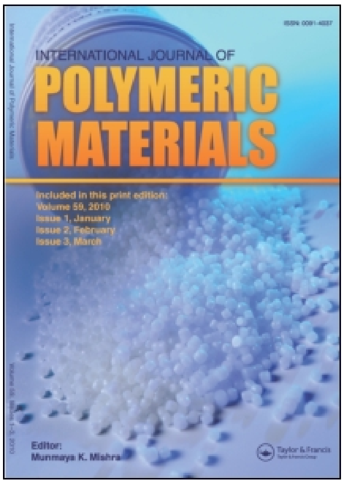

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

STUDIES ON THE MISCIBILITY OF POLY(2-HYDROXYETHYLMETHACRYLATE) AND HYDRODY PROPYL METHYL CELLULOSE BLENDS

K. Prashantha[a]; K. Vasanth Kumar Pai[a]; B. S. Sherigara[a]
[a] Department of Industrial Chemistry, Karnataka, India

To cite this Article Prashantha, K. , Pai, K. Vasanth Kumar and Sherigara, B. S.(2004) 'STUDIES ON THE MISCIBILITY OF POLY(2-HYDROXYETHYLMETHACRYLATE) AND HYDRODY PROPYL METHYL CELLULOSE BLENDS', International Journal of Polymeric Materials, 53: 6, 499 — 506

To link to this Article: DOI: 10.1080/00914030490450119

URL: http://dx.doi.org/10.1080/00914030490450119

International Journal of Polymeric Materials, 53:499–506, 2004
Copyright © Taylor & Francis Inc.
ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490450119

STUDIES ON THE MISCIBILITY OF POLY (2-HYDROXYETHYLMETHACRYLATE) AND HYDROXY PROPYL METHYL CELLULOSE BLENDS

K. Prashantha, K. Vasanth Kumar Pai* and B. S. Sherigara
Department of Industrial Chemistry, Kuvempu University,
Jnana Sahyadri Shimoga, Karnataka, India

Miscibility characteristics of poly[2-hydroxyethylmethacrylate] (PHEMA) and hydroxy propyl methyl cellulose (HPMC) have been investigated by solution viscometry, ultrasonic and differential scanning calorimetric (DSC) methods. The interaction parameters were obtained using the viscosity data. Ultrasonic velocity and adiabatic compressibilities versus blend composition have been plotted and are found to be linear. Variation of glass transition temperature (T_g) with composition follows the Gordon-Taylor equation. T_g values have also been calculated from the Fox equation. The results obtained reveal that PHEMA forms a miscible blend with HPMC over the entire composition range.

Keywords: polymer blend, miscibility, interaction parameters, ultrasonic velocity, glass transition temperature

INTRODUCTION

Polymer blends are physical mixtures of structurally different polymers that are interacting through secondary forces with no covalent bonding [1]. The importance of blending has increased recently because of their superior properties over homopolymers and can be compared to those of alloys over pure metals. The degree of compatibility usually determines the final properties of the blend [2]. The miscibility of the polymer blends can be determined by a number

Received 21 November 2001; in final form 3 December 2001.

One of the authors (KP) thanks the Kuvempu University authorities for the award of Research Fellowship.

Address correspondence to K. Vasanth Kumar Pai, Department of Industrial Chemistry, Kuvempu University, Jnana Sahyadri 577 451, Shimoga, Karnataka, India. E-mail: root@shikuv.kar.nic.in

of techniques, such as differential scanning calorimetry, neutron scattering, morphology studies by optical and electron microscopy, dynamic mechanical measurements, infrared spectroscopy, ultrasound and viscometry [3–8]. As a part of our studies on polymeric materials [9–11], in this article we report on the miscibility of a new blend system of Poly[2-Hydroxyethylmethacrylate] (PHEMA) and Hydroxy propyl methyl cellulose (HPMC). PHEMA and HPMC have been selected for the present study due to their pharmaceutical applications [12, 13].

EXPERIMENTAL

Polymers used in the present study PHEMA($M_w = 130000$) and HPMC(700 cps) were commercially supplied by Aldrich Chemical Company, Inc., USA. N,N dimethylformamide (DMF) was AR grade and was used as received.

For viscometric studies dilute solutions (2%w/v) were used. Stock solutions of PHEMA and HPMC and blend solutions at different compositions of 30/70, 50/50 and 70/30 were prepared in a common solvent DMF. Viscosity measurements were made using an Ubbelohde viscometer at 30°C.

Ultrasonic velocity of the blend solutions of 3% w/v was measured at 30°C using an ultrasonic pulse echo interferometer (SD UI-003) with a measuring frequency of 10 MHz. The accuracy of measurement was ±0.5%.

For DSC studies thin films of the component polymers and their blends with thickness in the order of microns were prepared by solution casting using DMF as the common solvent. Films were dried in vacuum for 48 hrs and were found to be transparent. The DSC measurements were made on a Mettler TA 4000 DSC in nitrogen atmosphere and the scan rate was 10 K/min.

RESULTS AND DISCUSSIONS

The measured values of viscosity, reduced viscocities of the homopolymers and their blends were found out. A plot of reduced viscosities of the component polymers and their 30/70, 50/50 and 70/30 blend compositions was found to be linear and no cross over was seen showing that the blends are compatible (Figure 1) [14, 15]. A sharp cross–over in the plots of reduced viscosity versus concentration is shown by incompatible blends [16].

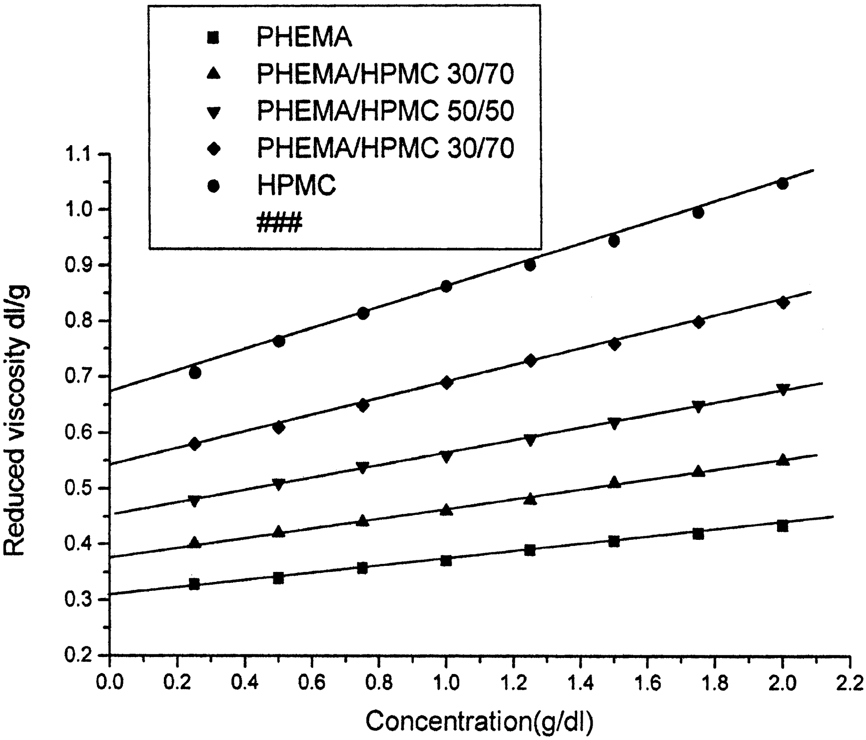

FIGURE 1 Reduced viscosity verses concentration of HPMC-PHEMA blends.

The interaction parameter ΔB of the blends was calculated using a Chee [14] expression when the polymers are mixed in weight fractions of w_1 and w_2 as

$$\Delta B = \frac{b - \bar{b}}{2w_1w_2} \tag{1}$$

where $\bar{b} = w_1b_{11} + w_2b_{22}$,
where b_{11} and b_{22} are the slopes of the viscosity curves for the pure components.

The coefficient b is related to the Huggins coefficient k_H as

$$b = k_H[\eta]^2 \tag{2}$$

For ternary system, the coefficient b is also given by

$$b = w_{12}b_{11} + w_{22}b_{22} + 2w_1w_2b_{12} \tag{3}$$

TABLE 1 Miscibility Parameters μ^a and α^b

Blend Composition PHEMA/HPMC	μ	α
0/100	–	–
30/70	0.1937	0.07972
50/50	0.2142	0.09280
70/30	0.1894	0.06253
100	–	–

[a] Using Chee [14] expression
[b] Using Sun [15] expression

If η_1 and η_2 are sufficiently apart, a more effective parameter μ can be used to predict the compatibility.

$$\mu = \frac{\Delta B}{([\eta]_2 - [\eta]_1)^2} \tag{4}$$

$\mu > 0$ signifies miscibility and $\mu < 0$ indicates phase separation. It is found that μ values are positive for all blend compositions predicting compatibility (Table 1).

Recently Sun et al. [15] suggested a new equation by considering the long–range hydrodynamic interactions for the determination of miscibility of polymers as follows:

$$\propto = k_m - \frac{k_1\eta_1^2 w_1^2 + k_2\eta_2^2 w_2^2 + \sqrt{2k_1k_2}[\eta]_1[\eta]_2 w_1 w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \tag{5}$$

where k_1, k_2 and k_m are the Huggins constants for individual pure components 1, 2 and blend, respectively. Sun et al. suggested that a blend will be miscible if $\propto \geq 0$ and immiscible when $\propto < 0$. In the present study $\propto$ values are positive for all blend compositions, indicating that blends are miscible (Table 1).

Ultrasonic velocity, density and adiabitic compressibility values of blends were found out. Adiabitic compressibility is calculated using the formula.

$$\beta_{nd} = \frac{1}{v^2\rho} \tag{6}$$

where v is the ultrasonic velocity and ρ is the density. Ultrasonic velocity of blends was plotted against blend compositions (Figure 2)

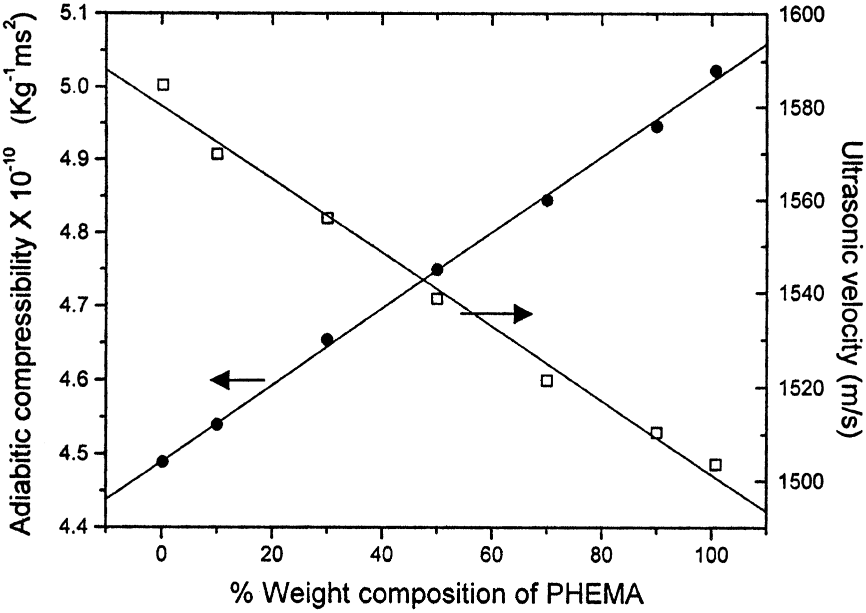

FIGURE 2 Ultrasonic velocity and adiabatic compressibility versus blend composition.

and found to be linear, which is the characteristic of compatible blends [17]. For incompatible blend solutions, ultrasonic velocity versus composition curve is non linear showing distinct phase inversion at intermediate composition. Adiabitic compressibility also varies linearly with blend composition (Figure 2).

The glass transition temperature (T_g) of homopolymers and their blends was recorded from DSC endotherms (Figure 3) and given in Table 2. Blends exhibit single T_g intermediate to those of PHEMA and HPMC. The Tg of miscible blend can be predicted using Fox equation [18] (equation 7) and Gordon-Taylor equation [19] (equation 8).

$$\frac{1}{T_g} = \frac{X_1}{T_{g1}} + \frac{X_2}{T_{g2}} \tag{7}$$

$$T_g = \frac{X_1 T_{g1} + k X_2 T_{g2}}{X_1 + k X_2} \tag{8}$$

where X_1, X_2, T_{g1} and T_{g2} are the weight fractions and glass transition temperatures corresponding to Polymer 1 and Polymer 2 respectively,

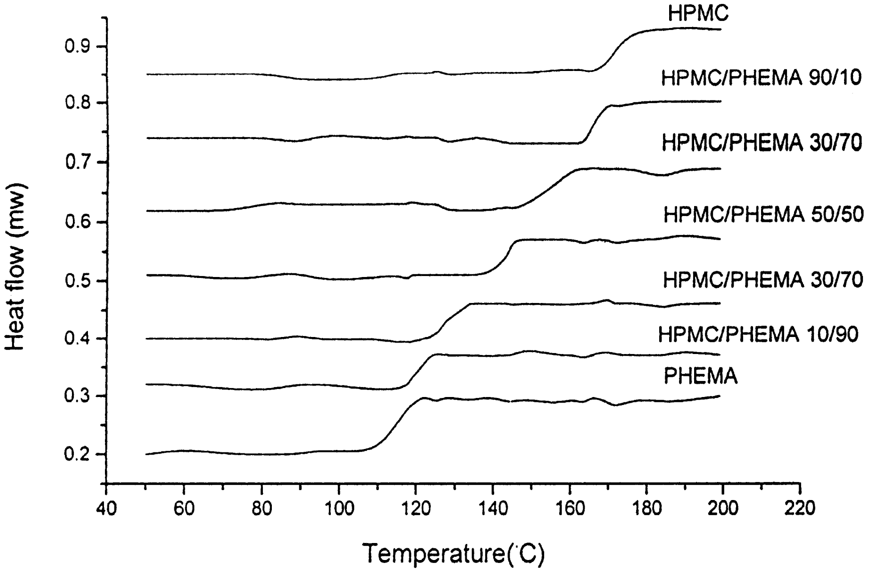

FIGURE 3 DSC thermograms of PHEMA-HPMC blends.

TABLE 2 Experimental and Theoretical Glass Transition Temperatures

Blend Composition PHEMA/HPMC	Experimental Tg(° C) values by DSC	Theoretical Tg(° C) values	
		Additive behavior	Fox equation
0/100	112	–	–
10/90	118	117	116
30/70	130	129	125
50/50	142	141	135
70/30	154	152	147
90/10	165	164	162
100/0	170	–	–

k is a constant that gives a semi-quantitative measure of the degree of interaction between two polymers. Tg values calculated from Fox equation and their theoretical values calculated from rule of mixtures are shown in Table 2. The blends show a positive deviation from Fox equation, implying an intermolecular interaction between the polymers. Slope (k) of the straight line obtained from Gordon-Taylor

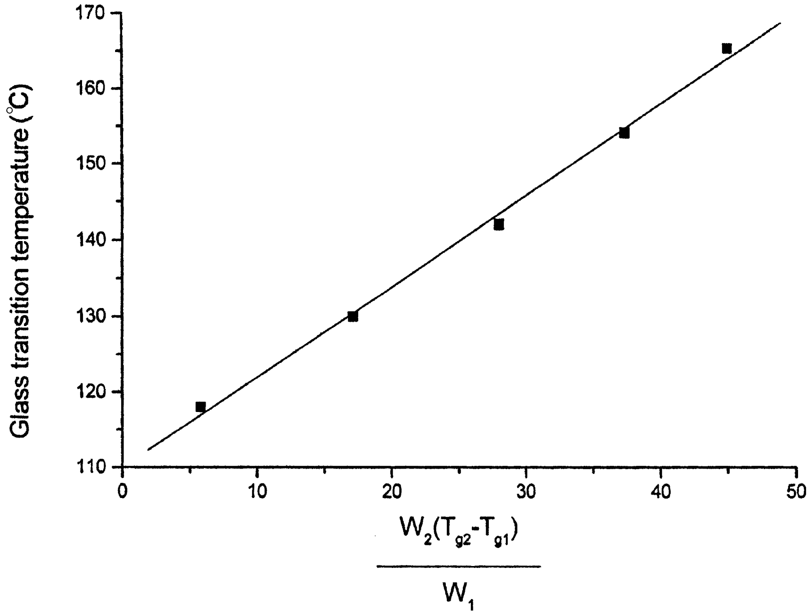

FIGURE 4 Verification of Gordon-Taylor equation for PHEMA-HPMC blends.

equation (Figure 4) was found to be 1.19. The Higher the value of 'k', the higher is the interaction.

CONCLUSIONS

The results obtained by viscosity, ultrasonic velocity and differential scanning calorimetry provide a clear indication that blends of Poly (2-hydroxyethylmethacrylate) with Hydroxypropylmethylcellulose are miscible over the whole composition range.

REFERENCES

[1] Shen, M. and Kawai, H. (1978). *AIChE J.*, **24**, 1.
[2] Krause, S. (1976). *J. Macromol.Sci.Rev: Macromol. Chem.* **7**, 251.
[3] Krause, S. (1978). In: *Polymer-polymer Compatibility in Polymer Blends*, Paul, D. R. and Newman, S. (Eds.), Academic Press, New York, 1.
[4] Singh, Y. P. and Singh, R. P. (1983). *Eur. Polym. J.* **19**, 535.
[5] Paramer, J. F., Dikinson, L. C., Chien, J. C. and Porter, W. (1989). *Macromolecules* **22**, 1078.
[6] Schenk, W., Reichert, D. and Schneider, H. (1990). *Polymer*, **31**, 329.
[7] Rao, V., Ashokan, P. V. and Sridhar, M. H. (1999). *Polymer*, **40**, 7167.
[8] Varadharajulu, A. and Reddy, R. L. (2000). *Intern. J. Polymeric. Mater.* **47**, 469.

[9] Prashantha, K., Vasanth Kumar Pai, K., Sherigara, B. S. and Prasannakumar, S. (2001). *Bull. Mater. Sci.* **24**, 535.

[10] Prashantha, K., Vasanth Kumar Pai, K. and Sherigara, B. S. (2001). *J. Appl. Polym. Sci.* (In press).

[11] Yashoda, M. P., Sherigara, B. S. and Venkateswaran, G. (2000). *Polymer*, **41**, 7381.

[12] Demircioglu, U., Beyenal, H., Tanyolac, A. and Hasirci, N. (1994). *Polym. Intl.*, **35**, 321.

[13] Wade, A. and Weller, P. J. (eds.), *Handbook of Pharmaceutical Excipients*; 2nd ed, (1994). *American Pharmaceutical Association*, Washington, 229−232.

[14] Chee, K. K. (1990). *Eur. Polym. J.*, **26**, 423.

[15] Sun, Z., Wang, W. and Fung, Z. (1992). *Eur. Polym. J.*, **28**, 1259.

[16] Dondos, A., Skondras, P., Pierri, E. and Benoit, H. (1983). *Macromol. Chem.* **184**, 2153.

[17] Singh, Y. P. and Singh, R. P. (1984). *E. Polym. J.* **20**, 201.

[18] Fox, T. G. (1956). *Bull. Am. Phys. Soc.* **1**, 123.

[19] Gordon, M. and Taylor, J. S. (1952). *J. Appl. Chem.* **2**, 493.