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Miscibility studies in poly(methyl vinyl ether)/hydroxypropylcellulose binary system in aqueous solutions and solid state

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Abstract

The phase separation behaviour in aqueous mixtures of poly(methyl vinyl ether) and hydroxypropylcellulose has been studied by cloud points method and viscometric measurements. The miscibility of these blends in solid state has been assessed by infrared spectroscopy; methanol vapours sorption experiments and scanning electron microscopy. The values of Gibbs energy of mixing of the polymers and their blends with methanol as well as between each other were calculated. It was found that in solid state the polymers can interact with methanol very well but the polymer–polymer interactions are unfavourable. Although in aqueous solutions the polymers exhibit some intermolecular interactions their solid blends are not completely miscible.

Keywords: Miscibility; Polymeric films; Lower critical solution temperature; Thermodynamics

1. Introduction

A combination of synthetic and natural polymers results in new materials, which have useful properties of synthetic component (good mechanical properties, easy processability, low production and transformation costs) and biocompatibility typical for biopolymers (Cascone et al., 2001; Cristallini et al., 2001). These blends have already been utilised as biodegradable biomaterials (Azevedo, Gama, & Reis, 2003), drug delivery systems (Cascone, Sim, & Downes, 1995), membranes (Yang, Su, Leu, & Yang, 2004), materials for agricultural application (Chiellini, Cinelli, Imam, & Mao, 2001), etc.

Polymers of vinyl ethers have recently attracted attention of various researchers due to a number of useful properties such as biocompartibility and non-toxicity, low glass transition temperatures, stimuli-responsive behaviour, etc. (Maeda, 2001; Matsumoto, Mazaki, & Matsuoka, 2004; Okabe, Sugihara, Aoshima, & Shibayama, 2002; Reyntjens & Goethals, 2001; Yun & Faust, 2002). However the studies on miscibility of poly(vinyl ethers) with other polymers are quite seldom except for the blends of poly(vinyl methyl ether) (PVME) with polystyrene and its derivatives (Lee & Sung, 2001; Pellerin, Prud'homme, & Pezolet, 2000; RamachandraRao & Watkins, 2000).

The blending of poly(vinyl ethers) with other water-soluble polymers can be of significant interest for design of materials for biomedical application. Cowie and co-workers (Cowie, Garay, Lath, & McEwen, 1989) have reported the preparation of blend films from poly(acrylic acid) and PVME by two different methods. The first approach included co-dissolution of polymers in methanol followed by solvent removal. In the second approach they mixed 0.2 M aqueous solutions of the polymers and observed precipitation of a polycomplex with the stoichiometry close to 1:1. The separated precipitate was hot-pressed at 97 °C to give tough, slightly yellow, but optically clear films. It was

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shown that in both cases the polymers formed completely miscible blends due to intermacromolecular hydrogen bonding. Earlier we reported the preparation of the blends based on poly(acrylic acid) and poly(2-hydroxyethyl vinyl ether) (Khutoryanskiy et al., 2003; Nurkeeva et al., 2004) and PVME (Nurkeeva et al., 2004) and demonstrated the possibility of their cross-linking by gamma-radiation. The blends were completely miscible, soft and elastic in a dry state and after cross-linking formed hydrogels upon immersion in water.

The intention of the present research was to prepare and characterise polymeric films by blending of PVME with water-soluble polysaccharide-hydroxypropylcellulose (HPC). Both PVME and HPC exhibit lower critical solution temperature (LCST) in aqueous solutions and it was interesting to know what happens with this feature in their mixtures. HPC is a typical polysaccharide and contains a large amount of hydroxyl-groups in its structure, which can act as a proton-donor with respect to proton-accepting ether groups of PVME and form intermacromolecular hydrogen bonding.

2. Experimental part

2.1. Materials

HPC with weight-average molecular weight M_W 370 kDa (Batch No 12807 MU) was purchased from Aldrich (USA). PVME with M_W 60 kDa was purchased from BASF (Lutonal M40, Germany). Both polymers were used without further purification.

2.2. Turbidity of solutions

The turbidity of HPC-PVME mixtures was measured using Shimadzu UV/VIS-2401 PC spectrophotometer (Japan) at the wavelength 400 nm. The temperature of solutions was regulated with the help of thermoelectrically temperature-controlled cell positioner CPS-240A (Shimadzu, Japan) in a heating regime. The accuracy of temperature regulation was ±1 °C. Before measurement every point was equilibrated for 10 min.

2.3. Viscosity measurements

The specific viscosity of solutions with different polymer ratios was measured with an Ubbelohde type viscometer with the flow time of distilled water 95 s at 25.0±0.2 °C.

2.4. Preparation of the films

For preparation of the films PVME and HPC were separately dissolved in water (with concentration of 0.1 unit. mol L^{-1}) and mixed at different molar ratios. The total volume was kept as 20 mL. The resulting mixture was dried on polyethylene plates with subsequent solvent evaporation for several days at room temperature. The films thickness was within 0.7–0.9 mm.

2.5. FTIR spectroscopy

The infrared spectra of the polymers were recorded in KBr discs using FTIR Spectrometer Mattson Satellite 3000 (USA).

2.6. Scanning electron microscopy

The morphological analysis of the films cross-sections was carried out using Superprobe 733 Electron Probe Microanalyzator (Jeol, Japan) at accelerating potential of 20 kV with the help of Inka Energy Scanning Spectrometer (Oxford Instrument, UK). The images were taken after coating with gold for 30 min in vacuum using Fine Coat Instrument (Jeol, Japan).

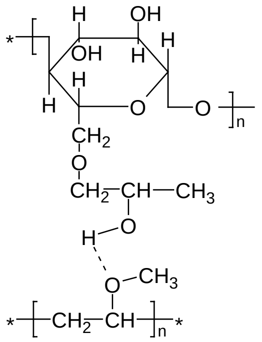
2.7. Methanol vapours sorption experiments

The sorption of methanol vapours by the polymeric films was studied using high-vacuum sorption apparatus (residual pressure 10^{-3} Pa) and McBain quartz-spring microbalance with a sensitivity of 0.3–0.5 m/kg. The spring extension was measured accurate to 5×10^{-6} m by V-630 cathetometer (Russia). In a typical experiment the polymer samples (with the weight of 0, 12–0, 15 g) were placed into a sorption apparatus and dried to a constant weight during 2–3 days at a high vacuum. Then the weight variant of isothermal interval sorption method was used according to Suvorova, Tyukova and Khasanova (2001). Methanol vapour pressure was measured by an OM-2 (Russia) pressure-gauge with the accuracy of 0.1%. The error in determination of vapour sorption in this experiment was no greater than 2%. All experiments were performed at 25 °C.

3. Results and discussion

3.1. Phase behaviour and interactions in aqueous solutions

Recently Starovoytova and co-workers (Starovoytova, Spevacek, Hanykova, & Ilavsky, 2004) have reported the presence of two phase transitions in aqueous mixtures of PVME and poly(*N*-isopropylmethacrylamide) at polymer concentrations $C=0.1$–10 wt% at temperatures roughly corresponding to different LCST typical for the individual polymers. This indicates that in the first approximation the single components undergo the phase transitions separately without the influence of a second polymer. These observations can be justified by the fact that both poly(*N*-isopropylmethacrylamide) and PVME can act as a proton-accepting polymers only and cannot interact with each other via hydrogen bonding. Unlike poly(*N*-isopropylmethacrylamide) our second polymer hydroxypropylcellulose has many hydroxyl-groups in its structure, which can act as proton-donating sites with respect to proton-accepting groups of PVME and form intermolecular hydrogen bonds. Schematically this interaction can be shown as follows:



Even though HPC has weaker proton-donating ability compared to poly(acrylic acid) we expected that the hydrogen bonding may affect the temperature induced phase separation behaviour in the mixtures of these polymers. Fig. 1 shows the dependence of solution turbidity on temperature for mixtures with different content of HPC. It can be clearly seen that the cloud point temperature of pure PVME is observed at 35 °C, which is in good agreement with the results of Starovoytova et al. (Starovoytova et al., 2004) and of pure HPC is at 42–43 °C. The mixtures of these polymers exhibit only one cloud point temperature, which depends on the polymers ratio. These observations lead us to conclusion that HPC and PVME interact with each other.

The interactions of proton-accepting poly(vinyl pyrrolidone) and poly(ethylene oxide) with water-soluble dextrin, dextran and inulin were previously reported by Ohno and co-workers (Ohno, Takinishi, & Tsuchida, 1981), who have applied viscometry as one of the most simple and convenient tool to monitor the conformation behavior of polymers. It was found that the interaction is accompanied by decrease in solution viscosity. We have applied the same approach to study the interactions between PVME and HPC (Fig. 2). The temperature of viscometric measurements was 25.0 ± 0.2 °C, which is below the phase transition temperature of both polymers. The reduced viscosity of pure PVME solution is quite low (0.296 dL/g) due to the fact that the macromolecules of this polymer are very flexible and its molecular weight is not high. An addition of the first portion of HPC (10%) to the solution of PVME is accompanied by a sharp increase in viscosity, which is likely due to the contribution of rigid macromolecules of HPC, which viscosity is high enough. The further increase in HPC content decreases the viscosity until 40 wt% of HPC in the mixture, which evidences the association between the two polymers via hydrogen bonding accompanied by a partial blockade of hydrophilic groups. Then the further addition of HPC leads to an increase in viscosity again associated with the presence of excessive HPC macromolecules. This viscosity dependence with a minimum is typical for binary polymer system with specific interactions (Ohno et al., 1981). The minimum of viscosity corresponds to the stoichiometry of the interaction product.

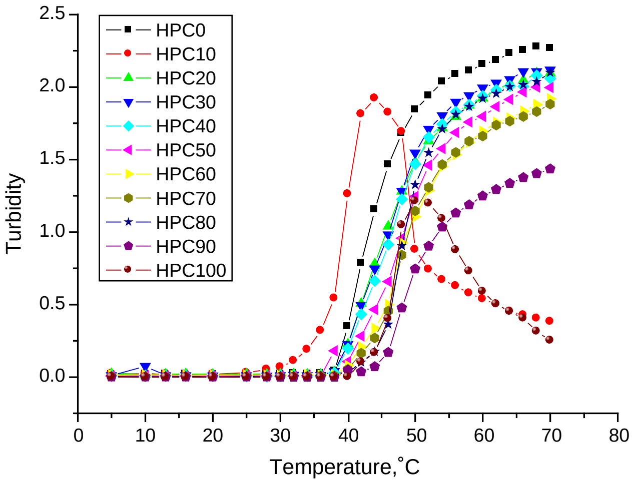


Fig. 1. Dependence of solution turbidity on temperature for pure PVME, pure HPC and their mixtures. $C_{polymers} = 0.05$ wt%.

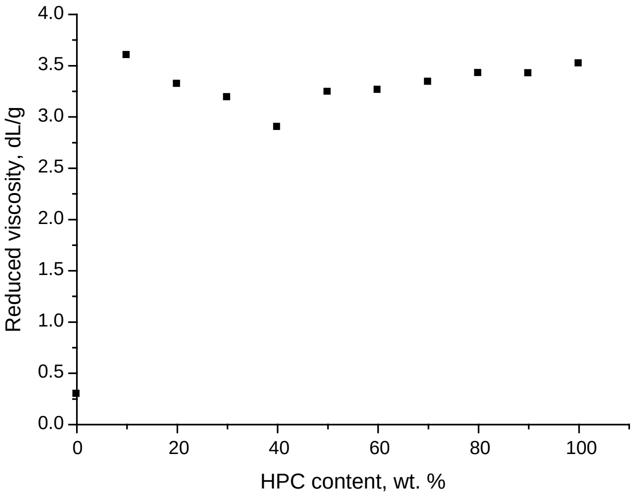


Fig. 2. Dependence of reduced viscosity on the content of HPC in PVME-HPC mixture. $C_{polymers} = 0.05$ wt%.

3.2. Characterisation of polymeric films based on PVME-HPC

The polymer films were prepared by casting the mixtures of PVME-HPC onto polyethylene plates and evaporation of water on air for several days. It should be noted that the blends containing more than 50 wt% of PVME were very adhesive and sticky and could not be detached from the polyethylene surface without mechanical damage. This is due to glue-like properties of pure PVME, which glass transition temperature is very low (−34 °C) and it does not form polymeric films with satisfactory mechanical characteristics (Molyneux, 1983). Taking it into consideration we

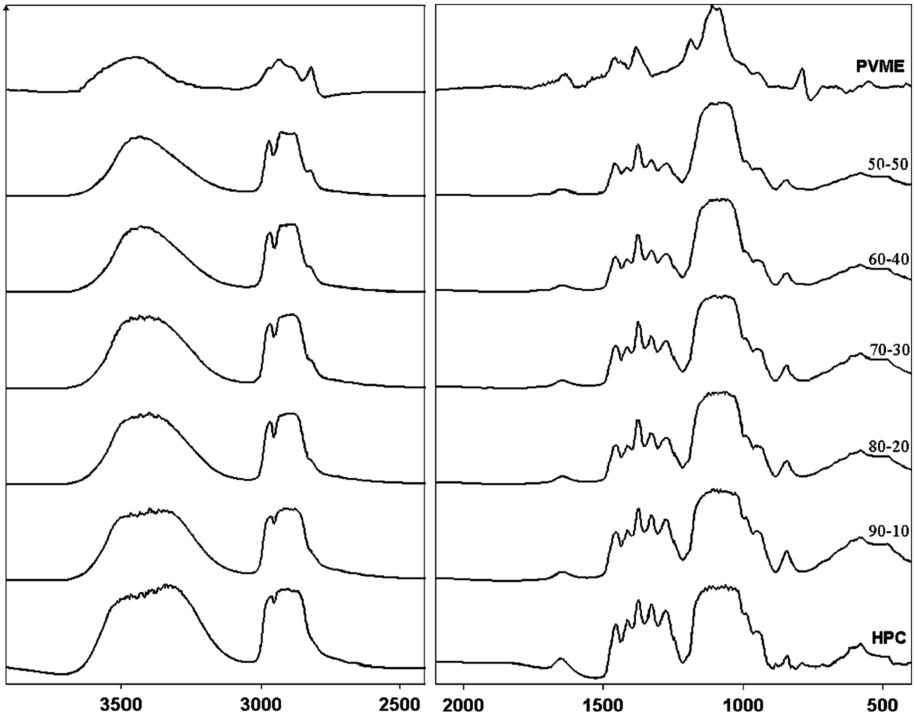


Fig. 3. FTIR spectra of PVME, HPC and their blends.

could not use these blends in our study. On the contrary the blends containing less than 50 wt % of PVME were relatively stable, elastic and transparent due to the contribution by HPC, which glass transition is about 40 °C (Khutoryanskiy et al., 2004) and its has excellent film forming and mechanical properties. These blends were used in our further investigations.

Fig. 3 shows the infrared spectra of HPC, PVME and the blends recorded in KBr discs. Two important regions can be distinguished in these spectra 3100–3600 and 1000–1200 cm^{-1}, responsible for vibrations of OH-groups of HPC and C–O–C bonds of both polymers. The presence of the broad peak at 3250–3600 cm^{-1} in the spectrum of pure PVME is an indication on the presence of water, which was not eliminated completely. It can be seen from the spectra that the intensity and the shape of the peaks depends on the polymers ratio in the blend. No significant broadening or shifting of the peaks is observed, which may indicate on relatively low concentration of intermolecular hydrogen bonds between the polymers.

The investigation of HPC by scanning electron microscopy (SEM) has shown (Fig. 4) that the morphology of this film is homogeneous. An addition of PVME to HPC changes the morphology of the materials dramatically. The appearance of different cavities and surface roughness in the morphology of the blends may be an indication that the polymers are not completely miscible. Nevertheless compared to the morphology of fully immiscible blends, for example, between HPC and poly(sodium acrylate) reported in our previous publication (Khutoryanskiy et al., 2004) the HPC-PVME blends do not show any sign of phase separation and interface boundaries.

3.3. Sorption of methanol vapours by HPC-PVME films

The thermodynamic condition for a complete miscibility in polymeric blends is a negative Gibbs energy of mixing $\Delta g_m < 0$ (He, Zhu, & Inoue, 2004). Therefore, the estimation of this value and its dependence on the composition of the system is of great importance because it gives information about the thermodynamic affinity between the components (thermodynamic compatibility) and thermodynamic stability of the system (Tager, Scholokhovich, & Bessonov, 1975).

Earlier Tager and co-workers (Tager et al., 1975) have reported the method for determination of free energy of mixing of two polymers by investigation of the sorption of organic solvent vapours by individual polymers and their mixtures. Later this method has been employed for determination of thermodynamic compatibility between different polymeric pairs (Suvorova, Tyukova, & Khasanova, 2001; Suvorova et al., 2002; Tyukova et al., 2002). In the present study we have used this method for estimation of the thermodynamic compatibility of HPC with PVME in the blends. Methanol was selected as a suitable solvent for this investigation due to its volatile nature as well as good ability to interact with both polymers. Fig. 5 shows the sorption isotherm of methanol by PVME, HPC and their blends. From the sorption data obtained we have calculated the changes in the chemical potential of methanol $\Delta\mu_1$ during

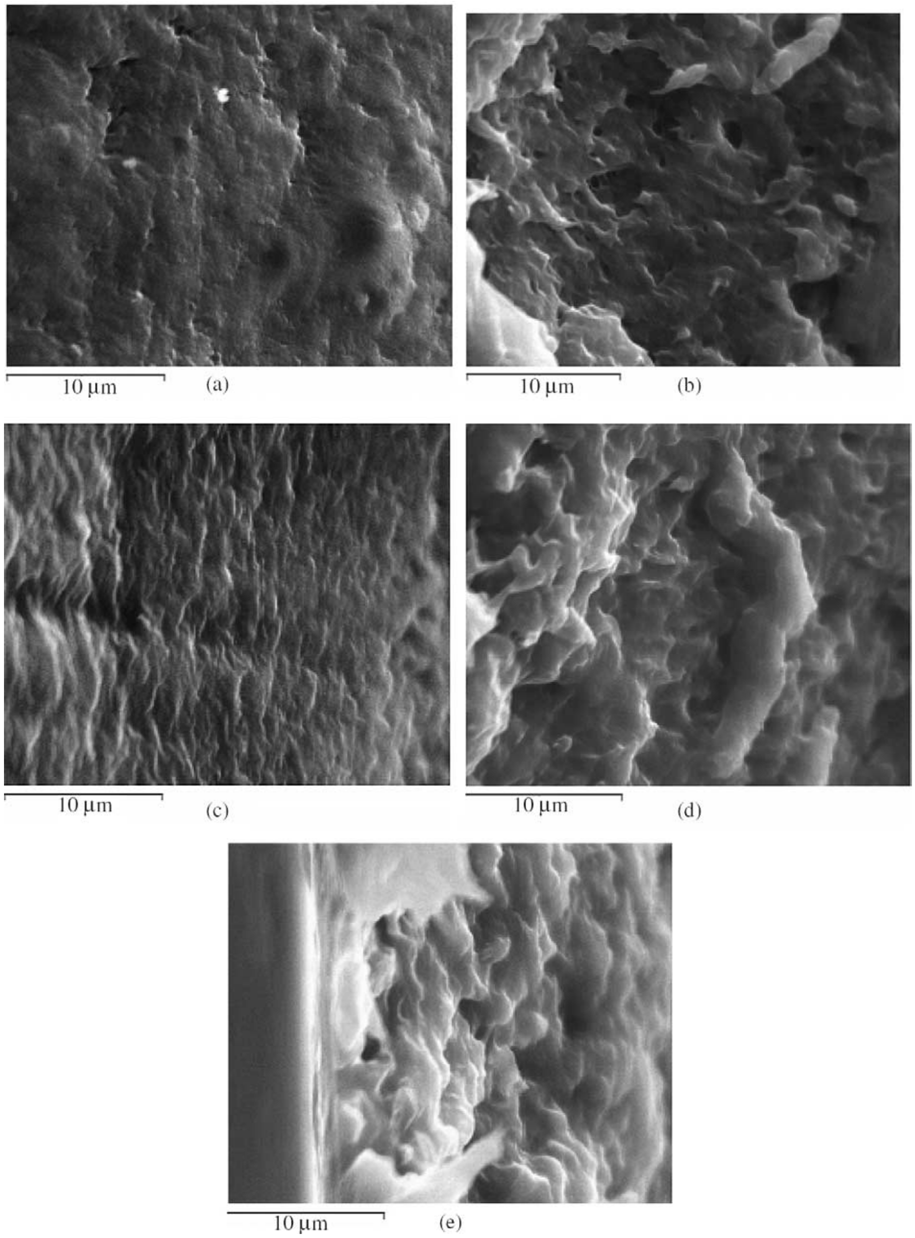


Fig. 4. SEM images of HPC (a) and blends containing 90 (b), 80 (c), 70 (d) and 60 wt % HPC (e).

the sorption using the following equation:

$$\varDelta\mu_1 = (R \times T/M_1) \times \ln p/p_s, \qquad (1)$$

where R is the Gas constant 8.315 J K^{-1} mol^{-1}, T is the absolute temperature (K), M_1 is the molecular weight of methanol and p/p_s is the partial pressure of the solvent (methanol).

The changes in the chemical potential of a polymer $\Delta\mu_2$ were calculated according to procedure described in Tager et al. (1975) using the Gibbs–Duhem equation:

$$\omega_1(\delta\Delta\mu_1/\delta\omega_1) + \omega_2(\delta\Delta\mu_2/\delta\omega_1) = 0 \qquad (2)$$

where ω_1 and ω_2 are the weight fractions of the solvent and polymer, respectively.

The average Gibbs energy of mixing of PVME, HPC and their blends with methanol were calculated using the following equation:

$$\Delta g_x = \omega_1 \times \Delta\mu_1 + \omega_2 \times \Delta\mu_2 \qquad (3)$$

The results of these calculations are presented in Fig. 6 as a dependence of Δg_x on the weight fraction of the polymer ω_2 (HPC) in the polymer blend. It can be seen that all curves are in the region of negative Δg_x values, which is an indication on the good ability of the polymers and the blends to interact with methanol. It is clearly seen that PVME exhibits the lowest affinity towards methanol. An addition of HPC to PVME increases the affinity of these blends to methanol sorption, which is probably due to the formation

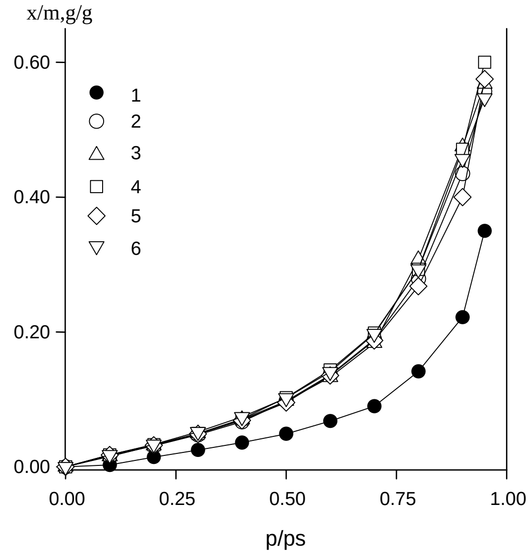


Fig. 5. Sorption isotherm of methanol by PVME (1), HPC (2) and polymer blends containing 60 (3); 70 (4); 80 (5); 90 wt% of HPC (6).

of cavities and morphology irregularities shown in the previous section by scanning electron microscopy. However the affinity to the solvent is prevalent in the polymer blends, which is typical for binary polymer blends with poor affinity between the components.

The values of the Gibbs energy of the polymer mixing in the blend (Δg_m) were calculated using the thermodynamic cycle using the data of Fig. 6. The values of Δg_1, Δg_2 and Δg_3 are the Gibbs energy of mixing of PVME, HPC and their blends with methanol are equal to segment that severed by the tangent to the curves of $\Delta g_x = f(\omega_2)$ at $\omega_2 = 1$. Then the value of Gibbs energy calculated per *g* of polymer component was estimated by the following equation:

$$-\Delta g_m = \Delta g_3 - (\omega_1 \times \Delta g_1 + \omega_2 \times \Delta g_2) \tag{4}$$

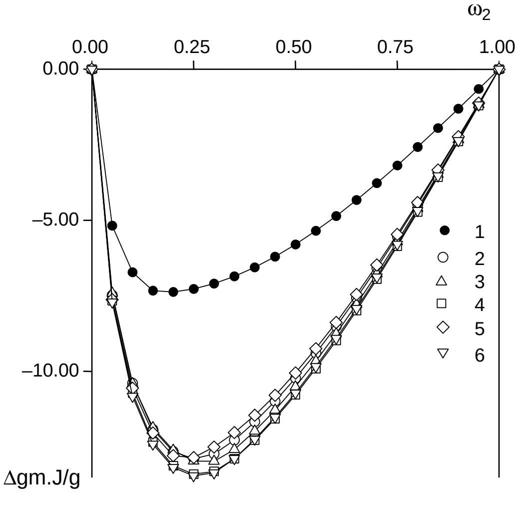


Fig. 6. Gibbs energy of mixing of HPC, PVME and their blends with methanol. Content of HPC in the sample: 0 (1), 100 (2), 60 (3); 70 (4); 80 (5); 90 wt% (6).

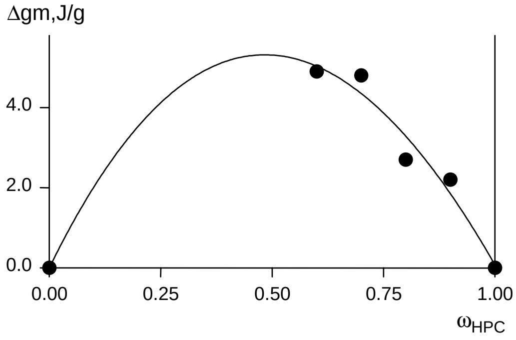


Fig. 7. Gibbs energy of mixing PVME with HPC.

These Δg_m values are plotted in Fig. 7 against the weight fraction of HPC in the blend. It is seen that the Gibbs energy of the polymer mixing are positive for the blends of all studied compositions, which is an indication on the thermodynamic immiscibility of PVME and HPC in solid state.

4. Conclusions

The mixing of hydroxypropyl cellulose with poly(vinyl methyl ether) in aqueous solutions results in their association, which affects the viscosity of the system and their phase separation temperature. The nature of these interactions may involve hydrogen bonding and hydrophobic effects.

The polymeric films can be prepared by blending of hydroxypropyl cellulose with poly(vinyl methyl ether) and casting from aqueous solutions. These films are clear and elastic. However the investigation of their thermodynamic compatibility reveals the immiscibility of the polymers in the solid blend. The polymers in the blend can interact with methanol very well but the polymer-polymer interactions are unfavourable. The thermal and mechanical investigation of these films is in progress and will be reported in our ongoing publications.

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References

Azevedo, H. S., Gama, F. M., & Reis, R. L. (2003). In vitro assessment of the enzymatic degradation of several starch based biomaterials. *Biomacromolecules*, *4*, 1703–1712.

Cascone, M. G., Sim, B., & Downes, S. (1995). Blends of synthetic and natural polymers as drug delivery systems for growth hormone. *Biomaterials*, *16*, 569–574.

Cascone, M. G., Barbani, N., Cristallini, C., Giusti, P., Ciardelli, G., & Lazzeri, L. (2001). Bioartificial polymeric materials based on polysaccharides. *Journal of Biomaterials Science. Polymer Edition*, *12*, 267–281.

Chiellini, E., Cinelli, P., Imam, S. H., & Mao, L. (2001). Composite Films Based on Biorelated Agro-Industrial Waste and Poly(vinyl alcohol). Preparation and Mechanical Properties Characterization. *Biomacromolecules*, *2*, 1029–1037.

Cowie, J. M. G., Garay, M. T., Lath, D., & McEwen, I. J. (1989). Formation of polymer-polymer complexes and blends in the system poly(acrylic acid)-poly(vinyl methyl ether). *British Polymer Journal*, *21*, 81–85.

Cristallini, C., Barbani, N., Giusti, P., Lazzeri, L., Cascone, M. G., & Ciardelli, G. (2001). Polymerisation onto Biological Templates, a New Way to Obtain Bioartificial Polymeric Materials. *Macromolecular Chemisty and Physics*, *202*, 2104–2113.

He, Y., Zhu, B., & Inoue, Y. (2004). Hydrogen bonds in polymer blends. *Progress of Polymer Science*, *29*, 1021–1051.

Khutoryanskiy, V. V., Cascone, M. G., Lazzeri, L., Barbani, N., Nurkeeva, Z. S., Mun, G. A., Bitekenova, A. B., & Dzhusupbekova, A. B. (2003). Hydrophilic films based on blends of poly(acrylic acid) and poly(2-hydroxyethyl vinyl ether): Thermal, mechanical and morphological characterization. *Macromolecular Bioscience*, *3*, 117–122.

Khutoryanskiy, V. V., Cascone, M. G., Lazzeri, L., Barbani, N., Nurkeeva, Z. S., Mun, G. A., & Dubolazov, A. V. (2004). Morphological and thermal characterization of interpolymer complexes and blends based on poly(acrylic acid) and hydroxypropylcellulose. *Polymer International*, *53*, 307–311.

Lee, S., & Sung, C. S. P. (2001). Surface chemical composition analysis in polystyrene/poly(vinyl methyl ether) blend films by UV reflection spectroscopy. *Macromolecules*, *34*, 599–604.

Maeda, Y. (2001). Spectroscopic Study on the Hydration and the Phase Transition of Poly(vinyl methyl ether) in Water. *Langmuir*, *17*, 1737–1742.

Matsumoto, K., Mazaki, H., & Matsuoka, H. (2004). Fluorinated Amphiphilic vinyl ether block copolymers: Synthesis and characteristics of their micelles in water. *Macromolecules*, *37*, 2256–2267.

Molyneux, P. (1983). *Water-Soluble Synthetic Polymers: Properties and Behavior*. V.1. Florida: CRC Press.

Nurkeeva, Z. S., Mun, G. A., Khutoryanskiy, V. V., Bitekenova, A. B., Dzhusupbekova, A. B., & Park, K. (2003). Soluble and cross-linked hydrophilic films based on compositions of poly(acrylic acid) with poly(2-hydroxyethyl vinyl ether) for controlled drug release. *Journal of Applied Polymer Science*, *90*, 137–142.

Nurkeeva, Z. S., Mun, G. A., Khutoryanskiy, V. V., & Dzhusupbekova, A. B. (2004). Hydrophilic films based on poly(acrylic acid)-poly(vinyl methyl ether) blends cross-linked by gamma-radiation. *Radiation Physics and Chemistry*, *69*, 205–209.

Ohno, H., Takinishi, H., & Tsuchida, E. (1981). Interpolymer complex formation of polysaccharides with poly(ethylene oxide) or poly(1-vinyl-2-pyrrolidone) through hydrogen bonding. *Macromolecular Chemisty Rapid Communication*, *2*, 511–515.

Okabe, S., Sugihara, S., Aoshima, S., & Shibayama, M. (2002). Heat-Induced Self-Assembling of Thermosensitive Block Copolymer 1. Small-Angle Neutron Scattering Study. *Macromolecules*, *35*, 8139–8146.

Pellerin, C., Prud'homme, R. E., & Pezolet, M. (2000). Orientation and Relaxation Study of Miscible Polystyrene/Poly(vinyl methyl ether) Blends. *Macromolecules*, *33*, 7009–7015.

RamachandraRao, V. S., & Watkins, J. J. (2000). Phase Separation in Polystyrene-Poly(vinyl methyl ether) Blends dilated with compressed carbon dioxide. *Macromolecules*, *33*, 5143–5152.

Reyntjens, W. G. S., & Goethals, E. J. (2001). New Materials from poly(vinyl ethers). *Polymers for Advanced Technology*, *2*, 107–122.

Starovoytova, L., Spevacek, J., Hanykova, L., & Ilavsky, M. (2004). ^{1}H NMR study of thermotropic phase transitions in D_2O solutions of poly(*N*-isopropylmethacrylamide)/poly(vinyl methyl ether) mixtures. *Polymer*, *45*, 5905–5911.

Suvorova, A. I., Tyukova, I. S., & Khasanova, A. Kh. (2001). Thermodynamics of mixing of crystalline poly(ethylene oxide) with amorphous poly(acrylates) and poly(methacrylates). *Polymer Science A.*, *43*, 1261–1265.

Suvorova, A. I., Safronov, A. P., & Mel'nikova, O. A. (2002). Thermodynamic compatibility of starch and carboxymethyl cellulose sodium. *Polymer Science A*, *44*, 84–88.

Tager, A. A., Scholokhovich, T. I., & Bessonov, Ju. S. (1975). Thermodynamics of mixing of polymers. *European Polymer Journal*, *11*, 321–326.

Tyukova, I. S., Khasanova, A. Kh., & Suvorova, A. I. (2002). Structure and thermodynamic properties of poly(ethylene oxide) blends with linear poly(siloxanes). *Polymer Science A*, *44*, 593–597.

Yang, J. M., Su, W. Y., Leu, T. L., & Yang, M. C. (2004). Evaluation of chitosan/PVA blended hydrogel membranes. *Journal of Membrane Science*, *236*, 39–51.

Yun, J., & Faust, R. (2002). Synthesis and Characterization of Amphiphilic A3B3 Hetero Arm Star Copolymers: Poly(isobutylene3-star-methyl vinyl ether3). *Macromolecules*, *35*, 7860–7862.