Scientific paper

Morphology and Thermal Behaviour of Poly (methyl methacrylate-co –*N*-vinyl-2-pyrrolidone) / Poly (ethylene glycol) Semi-interpenetrating Polymer Networks Based on Hydrogen Bonding Interaction

Guoqin Liu,[1,*] Ziran Liu,[2] Wenjun Zou,[1] Zhengxin Li,[1] Jin Peng,[1] Wenxi Cheng[1] and Sankui Xu[1]

[1] *College of Material Science and Engineering, Henan University of Technology, Zhengzhou, 450007, China.*

[2] *School of Mechanical and Electrical Engineering, Henan University of Technology, Zhengzhou, 450007, China*

* *Corresponding author: E-mail: guoqin_liu@haut.edu.cn*

Received: 18-04-2009

Abstract

Based on hydrogen bonding interactions, poly(methyl methacrylate-co-*N*-vinyl-2-pyrrolidone) (P(MMA-co-VP)) networks and linear poly(ethylene glycol) (PEG) can form semi-interpenetrating polymer networks (semi-IPNs). The morphology and thermal behaviors of the P(MMA-co-VP)/PEG semi-IPNs was studied by FTIR, XRD, TEM, and DSC. In P(MMA-co-VP)/PEG semi-IPNs, when the molecular weight of PEG is no more than 1000 in the semi-IPNs, P(MMA-co-VP)/PEG semi-IPNs are a homogeneous amorphous phase; similarly, when the proportion of PEG is less than 50 wt%, P(MMA-co-VP)/PEG semi-IPNs are fully amorphous; otherwise, P(MMA-co-VP)/PEG semi-IPNs are a mixture of PEG in the crystalline state with P(MMA-co-VP) networks in the amorphous state.

Keywords: Hydrogen bonding, semi-interpenetrating polymer networks, poly(methyl methacrylate-co-*N*-vinyl-2-pyrrolidone), poly(ethylene glycol)

1. Introduction

Interpenetrating polymer networks (IPNs) are defined as a combination of two or more polymers in a network form, at least one of which is polymerized and/or crosslinked in the immediate presence of the ofher(s).[1] Interpenetrating polymerization represents an innovative approach to solving the problem of polymer incompatibility.[2–6]

There are a variety of combinations possible with IPNs resulting in a broad range of properties. The performance of IPNs is determined by the physical and chemical nature of the constitutive networks, the relative proportion of components, the physical interactions between constitutive networks, the IPNs preparation procedure, and so on,[7] which could be a promising bioengineering material for a broad application. Besides full IPNs, in which both components are crosslinked independently of each other, there are also other types of IPNs such as semi-IPNs.[8,9] Semi-IPNs have only one component crosslinked and can be used as biocompatible materials.[10]

Poly(*N*-vinyl-2-pyrrolidone) (PVP) is one of the most frequently investigated classes of materials for use in medicine and in other applications interfacing with biological systems. The principal reason for successful PVP application is its excellent biocompatibility with living tissues and extremely low cytotoxicity. PVP can form stable complexes with polyacids through hydrogen bonding and this kind of complexes is the most stable of the hydrogen bonded complexes.[11–14]

PVP can form stable complexes with PEG through hydrogen bonds between the carbonyl groups of PVP and the terminal hydroxyl groups of oligomeric poly(ethylene glycol) (PEG).[15–18] PEG was selected because of its physicochemical and biological properties that include favorable pharmacokinetics and tissue distribution and the ability to excrete through human kidneys when molecular weight is less than 6000.[19,20] On the other hand, poly(*N*-vinyl-2-pyrrolidone) (PVP) and poly(ethylene glycol) (PEG) contain only electron-donating groups in their repeat units. It is therefore no wonder that PVP has been shown to be immiscible with high molecular weight PEG.[21]

In this paper, we design poly(methyl methacrylate-co-*N*-vinyl-2-pyrrolidone) (P(MMA-co-VP))/PEG semi-IPNs for potential biomaterials, i.e., P(MMA-co-VP) networks and linear PEG based on hydrogen bonds interaction between PVP and PEG, different from the hydrogen bonds of our previous systems;[22,23] the maximum molecular weight of linear PEG is less than 2000 in semi-IPNs. As a comonomer with *N*-vinyl-2-pyrrolidone, methyl methacrylate (MMA) has been selected due to its hydrophobic character. In semi-IPNs, crystalline aggregates cannot be found, although PEG is a semicrystalline polymer.

2. Experimental Section

2. 1. Materials

Methyl methacrylate (MMA) and 2,2'-azobis(isobutyronitrile) (AIBN) were of analytical grade obtained from the Chengdu Reagent Factory. Ethylene glycol dimethacrylate (EGDMA) and *N*-vinyl-2-pyrrolidone (NVP) were purchased from Aldrich Chemical Co. MMA was distilled under reduced pressure before use. AIBN, used as a radical initiator, was recrystallized from ethanol solution. NVP was used as received and EGDMA was used as a cross-linker without further purification. Poly(ethylene glycol) (PEG) (Aldrich) with catalogue number-average molecular weights of 400, 600, 800, and 1000 (Aldrich) was dried by heating at 70 °C for 7 h under vacuum.

2. 2. Preparation

The P(MMA-co-VP)/PEG semi-IPNs were prepared by radical polymerization and crosslinking of 37.5–59.5 wt% MMA and 26 wt% NVP in the presence of 0.5 wt% 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator, 1–15 wt% ethylene glycol dimethacrylate (EGDMA) as a crosslinker, and 15–40 wt% linear PEG (MW: 400, 600, 800, 1000). The reaction mixture was bubbled with nitrogen for 15 min to remove the oxygen from the mixture, and then injected into the space between two glass plates separated by polyethylene spacers (3 mm thick). Reaction was carried out at 55 °C for 24 h. The characteristics of the prepared polymer are summarized in Table 1. All specimens were quenched and then dried under vacuum at room temperature for 10 days to remove unreacted monomers. The weight loss during the drying process was negligible indicating that the monomer-to-polymer conversion was nearly 100%. According to the formulations of PEG content and compositions of P(MMA-co-VP)/PEG semi-IPNs, these polymers were represented as A (molecular weight of PEG) series, B (content of PEG) series and C (cross-linking density of network) series, respectively.

Table 1. Characteristics of P(MMA-co-VP)/PEG semi-IPNs prepared and T_g.

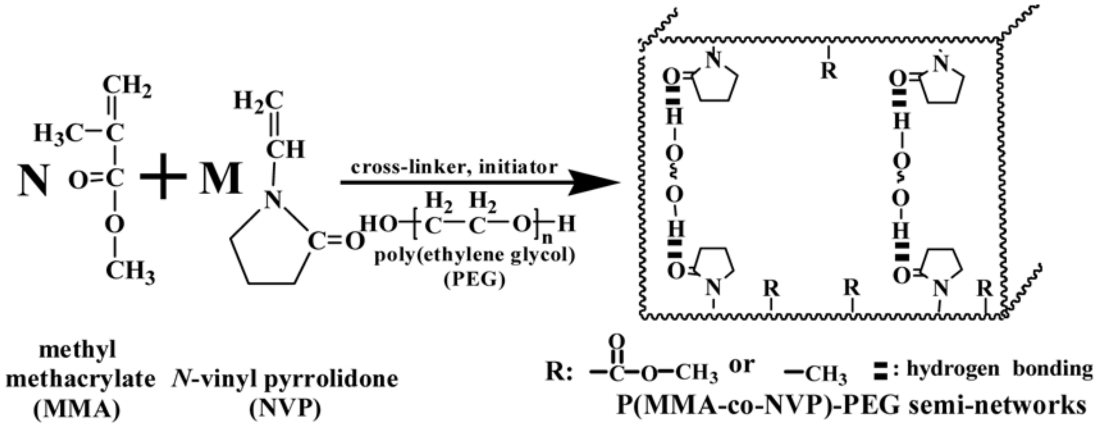
Notation	Cross-linking density (wt %)	PEG MW	PEG C (wt %)	T_g (°C)
A (Molecular weight of PEG) series				
A1	5.4	400	30	58
A2	5.4	600	30	62
A3	5.4	800	30	64
A4	5.4	1000	30	66
B (content of PEG) series				
B1	6.3	1000	15	91
B2	6.3	1000	30	82
B3	6.3	1000	35	74
B4	6.3	1000	40	64
C (Cross-linking density of network) series				
C1	1.0	1000	30	47
C2	3.7	1000	30	58
C3 (A4)	5.4	1000	30	66
C4	8.7	1000	30	78
C5	11.8	1000	30	98

2. 3. Measurements

FTIR spectra were obtained on a Nicolet 200XV FTIR spectrometer at a resolution of 2 cm^{-1}. A minimum of 16 scans were signal averaged. The dried samples were examined as pressed KBr disks. Various molecular weight PEG homopolymer can form spherulites. The spherulitic and oriented morphologies were observed and photographed through a polarizing optical microscope (POM) equipped with a digital camera and a heating stage. TEM measurements were carried out on a JEM-100CX Microscopy (Japan Electronic Company). Samples were prepared by dropping a suspension onto formvar-coated copper grids. X-ray scattering curves were obtained with a Philips X'pert Pro MPD, using Ni-filtered CuKa radiation. The thermal analyses were carried out with a differential scanning calorimeter (DuPont 9900) over a temperature range from –70 °C to 150 °C at a heating rate of 10 °C/min, purged with nitrogen gas, and quenched with liquid nitrogen. The cell was calibrated using an indium standard; the weight of the sample was 5–10 mg.

3. Results and Discussion

Poly (MMA-co-VP) networks were prepared and crosslinked by radical copolymerization of MMA with NVP in the presence of linear PEG. The obtained P(MMA-co-VP)/PEG is a kind of a semi-interpenetrating polymer networks,[24] i.e. crosslinked P(MMA-co-VP) network and linear PEG. Scheme 1 shows the synthesis route



Scheme 1 Synthesis of P(MMA-co-VP)/PEG semi-IPNs.

and the expected structure of P(MMA-co-VP)/PEG semi-IPNs.

It is well known that PEG is a semicrystalline polymer with higher crystallinity, as shown in Figure 1, however, in P(MMA-co-VP)/PEG semi-IPNs it can be observed that, up to concentration of 45 wt% of PEG, the sample is optically transparent at room temperature and the crystal cannot be observed by POM, indicating that P(MMA-co-VP)/PEG semi-IPNs are fully amorphous. When the proportion of PEG exceeds 50 wt%, the phase separations seriously occur in the seim-IPNs and the polymer is very fragile and unsuitable for use as a material. So, for the concentration of PEG used in this study, its content is no more than 45 wt%.

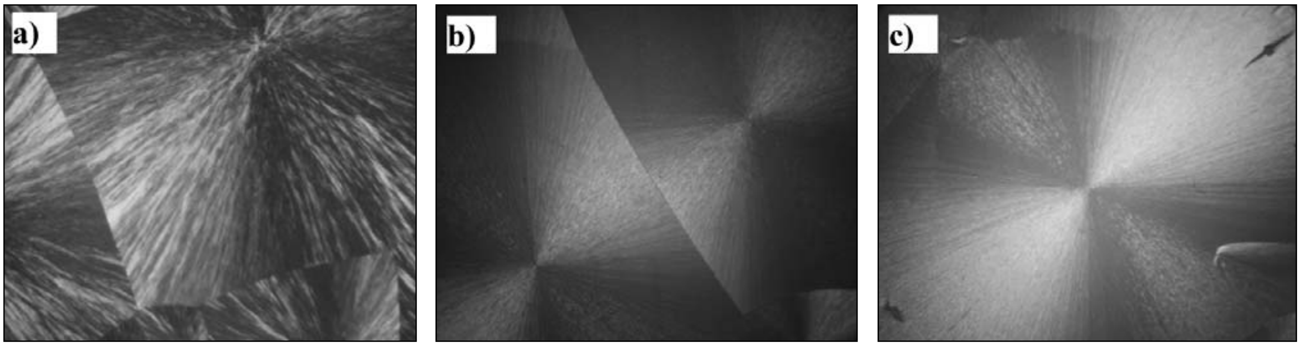


Figure 1 Polarizing optical microscopy (POM) of a) PEG1000; b) PEG800 and c) PEG600.

In further experiments, we have studied the influence of the H-bond interaction on P(MMA-co-VP)/PEG semi-IPNs. FTIR was used to characterize the H-bond interaction between PVP and PEG. Carbonyl group on PVP and hydroxyl group on PEG are employed as hydrogen acceptor and donor, respectively. We pay special attention to absorption of OH group stretching vibrations, because these groups are most sensitive to hydrogen bonds. Figure 2 shows a typical FTIR spectra of linear PEG, P(MMA-co-VP) networks and P(MMA-co-VP)/PEG semi-IPNs. For pure PEG600 (PEG, MW = 600) and PEG1000, it can be seen in Figure 2, that the OH vibration presents a broad band centered around 3354 cm^{-1} and 3359 cm^{-1}; the band corresponding to the absorption of a free OH group at 3640 cm^{-1} is absent in the PEG spectra.[25] This is because all hydroxyl groups of PEG form hydrogen bonds (intra- or intermolecular) and the hydrogen bond formation results form the interaction between the end hydroxyl and ether oxygen of the main chain, which makes the OH vibration shift to higher frequencies. For P(MMA-co-VP)/PEG semi-IPNs, compared to linear PEG, the OH vibration is shifted to a longer wavenumber of 3438 cm^{-1} for P(MMA-co-VP)/PEG600 semi-IPNs and of 3457 cm^{-1} for P(MMA-co-VP)/PEG1000 semi-IPNs, resulting from the H-bond between the PEG and PVP, forming a stronger hydrogen bond between PEG and PVP in the semi-IPNs than that in the pure PEG.

A second region in relation to hydrogen bonds is that of the carbonyl group in PVP and PMMA, which is also shown in Figure 1. For P(MMA-co-VP) networks, the vibration of PMMA and PVP carbonyl group appears around 1730 cm^{-1} and 1682 cm^{-1}, respectively. However, for P(MMA-co-VP)/PEG semi-IPNs, the frequency of the C=O stretching of the PVP is separated into two peaks

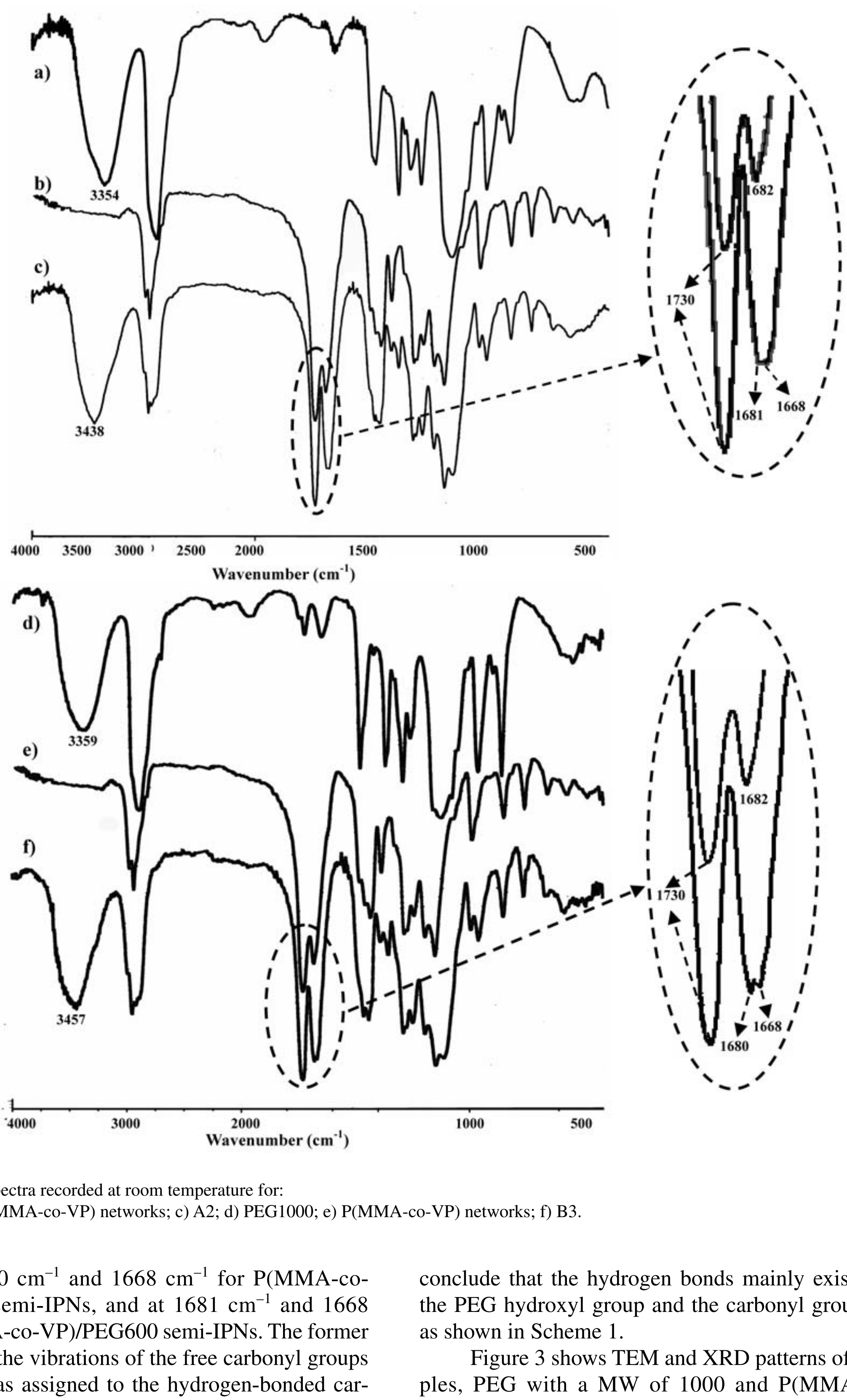


Figure 2. FTIR spectra recorded at room temperature for:
a) PEG600; b) P(MMA-co-VP) networks; c) A2; d) PEG1000; e) P(MMA-co-VP) networks; f) B3.

centered at 1680 cm^{-1} and 1668 cm^{-1} for P(MMA-co-VP)/PEG1000 semi-IPNs, and at 1681 cm^{-1} and 1668 cm^{-1} for P(MMA-co-VP)/PEG600 semi-IPNs. The former was assigned to the vibrations of the free carbonyl groups and the latter was assigned to the hydrogen-bonded carbonyl groups. It is noteworthy that the frequency of C=O stretching of the PMMA does not change, indicating that the carbonyl group of PMMA may not take part in the formation of the hydrogen bond. It can be reasonable to conclude that the hydrogen bonds mainly exist between the PEG hydroxyl group and the carbonyl group of PVP as shown in Scheme 1.

Figure 3 shows TEM and XRD patterns of two samples, PEG with a MW of 1000 and P(MMA-co-VP)/PEG1000 semi-IPNs (B4). It is obvious that pure PEG is crystalline at room temperature.

Because of its spherulitic structure, pure PEG can show its high and sharp X-ray peaks, as shown in Figure 3a

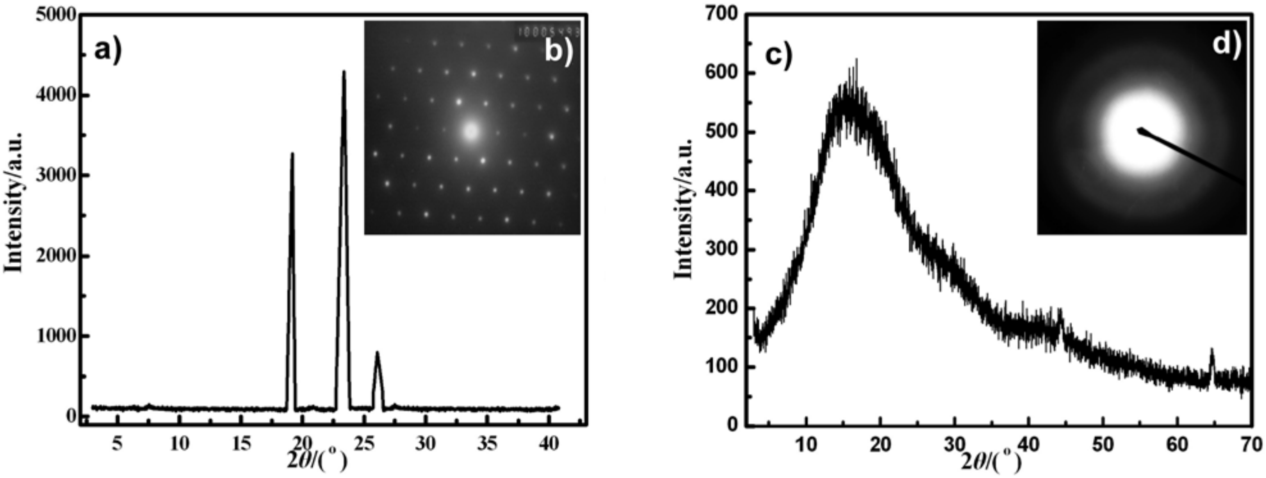


Figure 3. TEM diffraction photographs and XRD pattern.for:
a), b) PEG1000 homopolymer; c), d) P(MMA-co-VP)/PEG1000 semi-IPNs networks.

and typical crystal diffraction pattern by TEM observations, corresponding to regular lattice structure, as shown in Figure 3b.

However, PEG in semi-IPNs is amorphous. Figure 3c represents the XRD scattering patterns of the P(MMA-co-VP)/PEG1000 semi-IPNs and the X-ray peaks disappear. A broad, low-intensity peak is observed centered around 16°, suggesting that PEG in the semi-IPNs becomes completely amorphous and that these are fully miscible complexes with a homogeneous amorphous phase. In other words, the crystal structure of PEG has been changed by the procedure of blending. In Figure 3d P(MMA-co-VP)/PEG semi-IPNs shows an amorphous halo, indicating that the PEG molecules were dispersed in the amorphous phase and the characteristic of PEG crystal disappears; the P(MMA-co-VP)/PEG semi-IPNs are completely miscible. So we can come to the conclusion that the solid-solid phase change of the semi-IPNs in fact is a crystalline-amorphous transition of PEG in the blend. This is in agreement with the visual observations.

This is because the hydrogen bonds existing between PVP and PEG are in favor of the dispersion of PEG in P(MMA-co-VP) networks and can destroy the structure of PEG crystal aggregates; so, P(MMA-co-VP)/PEG semi-IPNs exhibit homogeneous amorphous phase; the PEG crystalline structure cannot be either observed via POM.

A simple and useful method to analyze the miscibility of PEG with P(MMA-co-VP)/PEG network is the determination of their glass transition temperatures (T_g) using DSC. The thermograms of the series A semi-IPNs, the series B semi-IPNs and the series C semi-IPNs are shown in the Figures 4–6, respectively. Only one transition is observed for all P(MMA-co-VP)/PEG semi-IPNs; a single compositionally dependent glass transition is an indication of full miscibility at a dimensional scale between 20 and 40 nm[26] and implies full miscibility of the semi-IPNs.

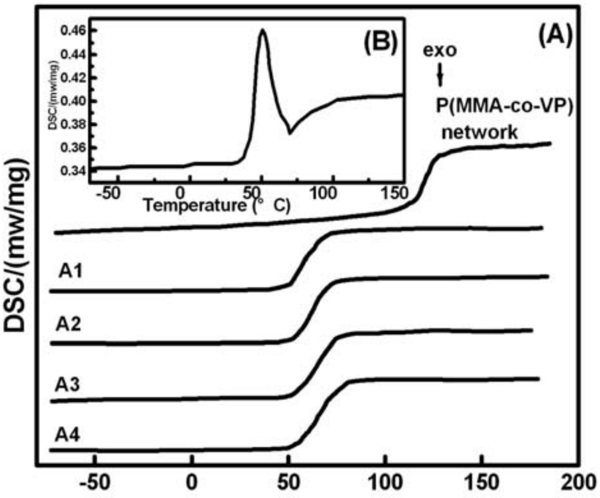


Figure 4 DSC scans of P(MMA-co-VP) networks and series A semi-IPNs with various molecular weight of PEG (A), P(MMA-co-VP)/PEG2000 (B).

It would be of interest to study the effects of the chain length of PEG on the complexation with the P(MMA-co-VP) networks. Figure 4A suggests that the pure amorphous P(MMA-co-VP) network exhibits one T_g at ca. 125 °C and the P(MMA-co-VP)/PEG semi-IPNs display a single T_g. The addition of PEG to P(MMA-co-VP) network causes the depression of the T_g of PMMA network; the smaller the molecular weight of PEG, the more the T_g is decreased. Comparing Figures 4A and 4B, when the molecular weight of PEG exceeds 1000, we learn that P(MMA-co-VP)/PEG semi-IPNs in fact are a mixture of PEG in the crystalline state with P(MMA-co-VP) networks in the amorphous state.

We have also studied the influence of the PEG content on P(MMA-co-VP)/PEG semi-IPNs. As shown in Figure 5A, pure PEG1000 only shows the melting temperature without T_g because PEG is easily crystallized and the

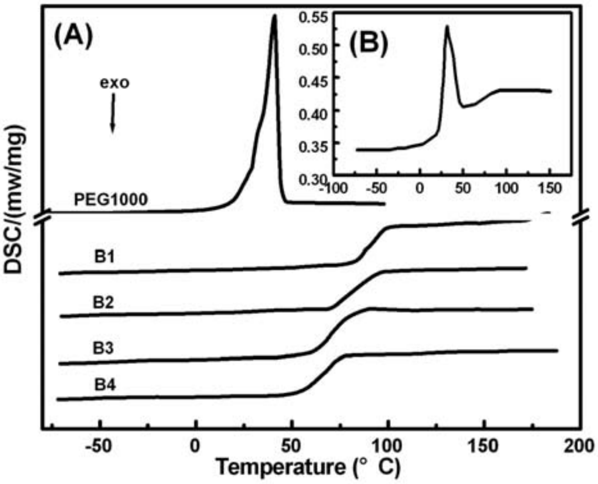


Figure 5. DSC scans of series B semi-IPNs with various content of PEG (A), P(MMA-co-VP)/PEG2000 (50:50 wt) semi-IPNs (B).

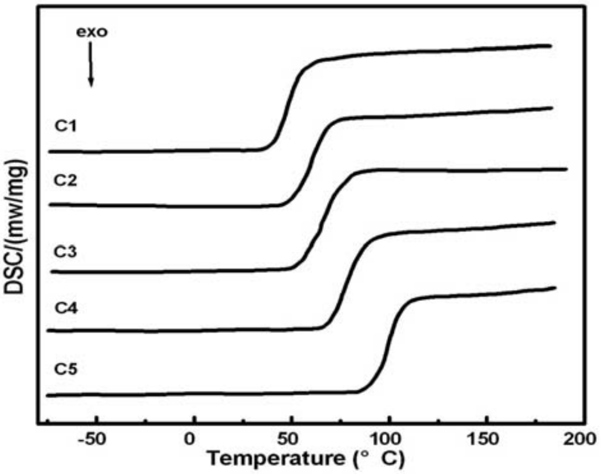


Figure 6. DSC scans of series C semi-IPNs with various cross-linking densities.

content of the amorphous phase is very low;[27] thus, it is very difficult to measure the T_g of PEG in general. However, endothermic peaks due to the melting of the PEG crystallites are not observed and only one glass transition was exhibited corresponding to the P(MMA-co-VP)/PEG1000 semi-IPNs. These facts mean that the crystalline phase of PEG1000 is destroyed in the complex and that there is only the amorphous phase in P(MMA-co-VP)/PEG semi-IPNs where the segments are molecularly mixed, in agreement with the TEM analysis. On the other hand, when the proportion of PEG exceeds 50 wt%, the semi-IPNs is also a mixture of PEG in the crystalline state with P(MMA-co-VP) networks in the amorphous state.. In the case of T_g of the semi-IPNs, it decreases with increasing of the PEG content, which may be interpreted in the terms of the Fox equation.

The influences of cross-linking density on P(MMA-co-VP)/PEG semi-IPNs are presented in Figure 6. It is worth noting that cross-linking density plays an important role for T_g of semi-IPNs. With the increase of cross-linking density of the polymer networks, T_g of the semi-IPNs shifts to relatively high temperature. It is known that several factors can influence the T_g values of the crosslinked polymers: main chain rigidity, crosslinking density and the chemical structure of the hardener introduced. Relatively high crosslinking densities restrict the motions of polymer chain and make T_g shift to a high temperature region.

4. Conclusion

Linear PEG and P(MMA-co-VP) networks can form the semi-IPNs by the hydrogen-bond between the PEG hydroxyl group and the carbonyl group of PVP, which could be confirmed by FTIR spectra. In P(MMA-co-VP)/PEG semi-IPNs, when the molecular weight of PEG is no more than 1000 in the semi-IPNs, P(MMA-co-VP)/PEG semi-IPNs are a homogeneous amorphous phase; similarly, when the proportion of PEG is less than 50 wt%, P(MMA-co-VP)/PEG semi-IPNs are fully amorphous; otherwise, P(MMA-co-VP)/PEG semi-IPNs are a mixture of PEG in the crystalline state with P(MMA-co-VP) networks in the amorphous state. The molecular weight of PEG, the content of PEG and the crosslinking density of P(MMA-co-VP) network have the important influence on the T_g of semi-IPNs; with the increase of the molecular weight of PEG and the cross-linking density, the T_g of semi-IPNs increases; but, the T_g of semi-IPNs decreases with the increasing of the content of PEG.

5. References

1. L. H. Sperling, V. Mishra, *Polym. Advan. Technol.* **1996**, *7*, 197–208.
2. S. J Park, J. S. Jin, *J. Appl. Po1ym. Sci.* **2001**, *82*, 775–780.
3. S. Desai, I. M. Thakore, Brennan, et a1., *J. Appl, Po1ym. Sci.* **2002**, *83*, 1576–1585.
4. V. Athawale, S. Ko1ekar, *J. Macromol. Sci. Pure Appl. Chem.* **2000**, *37*, 65–79.
5. H. X. Xiao, K. C. Frisch, H. L. Frisch, *J. Polym. Sci. Polym. Chem.* **1983**, *21*, 2547–2557.
6. H. X. Xiao, K. C. Frisch, H. L. Frisch, *J. Polym. Sci. Polym. Chem.* **1984**, *22*, 1035–1042**.**
7. A. Anžlovar, M. Žigon, *Acta Chim. Slov.* **2005**, *52*, 230–237.
8. A. Anžlovar, M. Žigon, *J. Polym. Sci. Part B: Polym. Phys.* **2002**, *40*, 115–123.
9. F. B. Calleja, E. G. Privalko, A. M. Fainleib, et a1., *J. Macromol. Sci. Phys.* **2000**, *39*, 131–141.
10. Y. Chen, D. Ding, Z. Mao, Y. He, Y. Hu, W. Wu, X. Jiang, *Biomacromolecules* **2008**, *9*, 2609–2614.
11. A. M. Lowman, N. A. Peppas, *Polymer* **2000**, *41*, 73–80.
12. S. Liu, X. Fang, Y. D. Hu, G. Gao, *J. Appl. Polym. Sci.* **2001**, *82*, 620–627.

13. E. A. Bekturov, V. A. Frolova, L. A. Bimendina, *Macromol. Chem. Phys.* **1999**, *200*, 431–435.
14. Y. Osada, *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17,* 3485–3488.
15. M. M. Feldstein, G. A. Shandryuk, N. A. Platé, *Polymer* **2001**,*42*, 971–979.
16. M. M. Feldstein, S.A. Kuptsov, G. A. Shandryuk,, N.A. Platé, *Polymer* **2001**,*42*, 981–990.
17. M. Novikov, A. Roos, C. Creton, M. Feldstein, *Polymer* **2003,** *44*, 3561–3578.
18. R. J. Sengwa, *Polym. Int*. **2003,** *52*, 1462–1467.
19. S. Zalipsky, J. M. Harris, Introduction to Chemistry and Biological Applications of Poly(ethylene glycol). In: Poly(ethylene glycol) Chemistry And Applications, ACS Symposium Series 680, ACS: Washington DC, **1997,** 1–13.
20. P. K. Working, M. S. Newman, J. Johnson, J. B. Cornacoff, Introduction to Chemistry and Biological Applications of Poly(ethylene glycol), ACS Symposium Series 680, ACS: Washington, DC, **1997,** 45–57.
21. L. Cesteros, J. Quintana, J. Fernandez, I. Katime, *J.Polym. Sci., Polym. Phys. Ed.* **1989,** *27*, 2567.
22. Y. P. Cao, G. Q. Liu, X. Y. Liu, X. B. Ding, Y. X. Peng, A. S. C. Chan, *New J. Chem.* **2003,** *18*, 2368–2372.
23. G. Liu, X. Ding, Y. Cao, Z. Zheng, Y. Peng, *Macromolecules* **2004,** *37*, 2228–2232.
24. L. H. Sperling, V. Mishra, *Polym. Advan. Technol.* **1996,** *7*, 197–208.
25. O. E. Philippova, S. I. Kuchanov, I. N. Topchieva, V. A. Kabanov, *Macromolecules* **1985,** *18*, 1628–1633.
26. S. W. Kuo, F. C. Chang, *Macromolecules* **2001,** *4*, 4089–4097.
27. N. K. Kafoglou, D. D. Sotiropoulou, A. G. Margaritis, *Eur. Polym. J.* **1988***,* *4*, 389–394.

Povzetek

Zaradi vodikovih vezi lahko poli(metil metakrilat-co-*N*-vinil-2-pirolidonske) (P(MMA-co-VP)) mreže in linearni poli(etilen glikol) (PEG) tvorita semi-interpenetrirajoča polimerna omrežja (semi-IPN). Morfološko in termično obnašanje P(MMA-co-VP)/PEG semi-IPN smo študirali z FTIR, XRD, TEM in DSC. V P(MMA-co-VP)/PEG semi-IPN, v katerih je molekulska masa PEG v semi-IPN manjša od 1000, so P(MMA-co-VP)/PEG semi-IPN v obliki homogene, amorfne faze; podobno je tudi, ko je delež PEG manjši od 50 wt%, in so P(MMA-co-VP)/PEG semi-IPN popolnoma amorfni; v drugih primerih so P(MMA-co-VP)/PEG semi-IPN v obliki zmesi PEG v kristaliničnem stanju in omrežij P(MMA-co-VP) v amorfnem stanju.