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Complexation of poly(ethylene glycol) with poly(ethyl methacrylate-co-N-vinyl--2-pyrrolidone) gel based on hydrogen bonds

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The complexes of poly(ethyl methacrylate-co-N-vinyl-2-pyrrolidone) (P(EMA-co-VP)) gel with poly-(ethylene glycol) (PEG) stabilized by the hydrogen bonds were prepared. It was found that both the concentration and the molecular weight of PEG have a strong effect on the P(EMA-co-VP) gel. When PEG was introduced into the P(EMA-co-VP) gel, the glass transition temperatures (T_g) of the complexes decreases with the decreasing of PEG molecular weight. In such a system, the maximum molecular weight of PEG required for the complex formation is no more than 2000, and P(EMA-co-VP)/PEG complexes are a homogeneous amorphous phase, which was studied by FTIR, XRD, TEM, and DSC.

Keywords: complex, hydrogen bonds, poly(ethyl methacrylate-co-N-vinyl-2-pyrrolidone) gel, poly(ethylene glycol).

INTRODUCTION

Polymer gels are three-dimensional polymeric networks[1, 2], and have an ability to react to the changes in external conditions by considerable volume changes, swelling or shrinkage, which results in the creation of a novel class of intelligent materials for advanced applications in biotechnology, medicine or industry[3–7]; the external conditions include not only temperature changes, but also a variation in the ionic strength, the pH value, or the quality of the solvent, and so on. Among them, the drastic shrinkage of gel volume as a result of the interaction between gel and different compounds is widely investigated[8–11], and those interpolymer complexes are formed through some secondary binding forces such as hydrogen bonding, Coulombic force, or hydrophobic interaction in aqueous medium[12–14].

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 reason for successful PVP application is their excellent biocompatibility with living tissues and extremely low cytotoxicity. PVP can form stable complexes with poly(ethylene glycol) (PEG) through hydrogen bonds between the carbonyl groups of PVP and the terminal hydroxyl groups of oligomeric PEG[15–18]. Hydrogen bond is a very important noncovalent interaction system, such as in an aqueous two-phase system[19–23]. 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[24]. 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[25].

In this paper, we design poly(ethyl methacrylate-co--N-vinyl-2-pynolidone)/ Poly(ethylene glycol) (P(EMA--co-VP)/PEG) complexes, i.e., P(EMA-co-VP) gel and linear PEG based on hydrogen bonds between PVP and PEG, which is appealing for biological applications, and the maximum molecular weight of linear PEG is no more than 2000. Due to its hydrophobic and flexible properties and the strong hydrophilic nature of PVP, ethyl methacrylate (EMA) has been selected as a comonomer with N-vinyl-2-pyrrolidone. In the complexes, crystalline aggregates cannot be found, although PEG is a semicrystalline polymer.

EXPERIMENTAL

Materials

Ethyl methacrylate (EMA) 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. EMA 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(ethy1ene glycol) (PEG) (Aldrich) with the catalogue number-average molecular weights of 400, 600, 800, 1000, 1500 and 2000 (Aldrich) was dried by heating at 70°C for 7 hr under vacuum.

Preparation

The P(EMA-co-VP) gel was prepared by radical copolymerization of 1.0 mol·L^{-1} EMA with 1.0 mol · L^{-1} NVP in the presence of 0.01 mol · L^{-1} AIBN as an initiator and EGDMA as a crosslinker in dimethyl sulfoxide. The reaction mixture was bubbled with nitrogen for 15 min. to remove the oxygen from the mixture, then injected into the space between two glass plates separated by polyethylene spacers (3 mm thick) or into a cylindrical glass tube with a diameter 7 mm. Gelation was carried out at 55°C for 24 hours. After polymerization, the crosslinked P(EMA-co-VP) was immersed in 2000 ml ethanol-water mixture (50/50 wt.%) for 1 week to remove the monomers and uncrosslinked polymers, then in a large amount water for 3 weeks, until equilibrium was reached. The sample was divided into two parts. One represented as P(EMA-co-VP) gel was still immersed into water. The other part was put in PEG solution (3 ml of the solution per 1 mg of swollen network). The formulations of initial PEG solution are summarized in Table 1. The

samples were thermostated at 25°C for 3 days, then the rinsed PEG absorbed on the surface of P(EMA-co-VP)/PEG complex with water. According to the formulations of PEG content and compositions of P(EMA-co-VP)/PEG complexes, these polymers were represented as A (molecular weight of PEG) series, B (content of PEG) series and C (cross-linking density of the network was simply calculated as the molar ratio of crosslinker to the total monomer) series, respectively. All specimens were dried under vacuum at room temperature for 7 days.

Composition of Complexes

To obtain the information on copolymer composition and polymer yield, a sample of the prepared gels was quenched and then dried under vacuum at room temperature for 10 days to remove solvent and unreacted monomers. The weight loss, except for the solvent, during the drying process was negligible indicating that the monomer-to-polymer conversion was nearly 100% and that the molar ratio of PEMA to PVP in the copolymer was close to 1:1. The composition of the complexes was characterized as follows: by knowing the weight of the dried P(EMA-co-VP) gel before complexation, the weight of the P(EMA-co-VP)/PEG complexes equilibrated with PEG water solution (the water on the surface of complex disks was adsorbed before weighing) and the weight of the dried P(EMA-co-VP)/PEG complexes, we could calculate the binding degree (θ: molar fraction of PEG/PVP repeating units in the networks) of PEG with the polymer network. The relative mass of the complex was characterized by m/m_0 ratio, where m is the mass of the P(EMA-co-VP)/PEG complex at the equilibrium state (It can be determined experimentally with satisfactory accuracy (about 3%)) and m_0 is the mass of the P(EMA-co-VP) gel equilibrated with water.

Table 1. Characteristics of P(EMA-co-VP)/PEG Complexes

Notation	Cross-linking density (mol %)	Formulation of initial PEG solution	
		MW	C_P^* (wt. %)
A (content of PEG) series			
A1	6	1000	1
A2	6	1000	5
A3	6	1000	7
A4	6	1000	11
A5	6	1000	15
A6	6	1000	20
A7	6	1000	25
A8	6	1000	30
A9	6	1000	35
A10	6	1000	40
B(Molecular weight of PEG) series			
B1	4	400	25
B2	4	600	25
B3	4	800	25
B4	4	1000	25
B5	4	1500	25
B6	4	2000	25
C (Cross-linking density of network) series			
C1	0.5	1000	30
C2	1	1000	30
C3	3	1000	30
C4	5	1000	30
C5	7	1000	30
C6	10	1000	30

*The initial concentration of PEG.

Measurements

The 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. The TEM measurements were carried out on a JEM-100CX Microscopy (Japan Electronic Company). The samples were prepared by dropping an aqueous suspension of cleaned material onto the 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.

RESULTS AND DISCUSSION

Poly (EMA-co-VP) gels were prepared and crosslinked by radical copolymerization of EMA with NVP, then was put in the solution of PEG. Complexes formed between PVP and PEG are stable complexes. This stabilization is attributed to the strong intermolecular affinity between the polymer chains, and the hydrogen bonding between PEG and PVP is mainly responsible for the interpolymer association. The carbonyl group on PVP and the hydroxyl group on PEG are employed as hydrogen acceptor and donor, respectively.

Figure 1 shows the infrared spectra of the carbonyl group in P(EMA-co-VP)/PEG1000 (PEG, molecular weights = 1000) complexes and P(EMA-co-VP) gel. For P(EMA-co-VP) gel, the vibration of PEMA and PVP carbonyl group appears around 1727 cm^{-1} and 1683 cm^{-1}, respectively. However, for P(EMA-co-VP)/PEG complexes, the frequency of the C=O stretching of the PVP is separated into two peaks centered at 1683 and 1662 cm^{-1} for P(EMA-co-VP)/PEG complexes. The former was assigned to the vibrations of free carbonyl

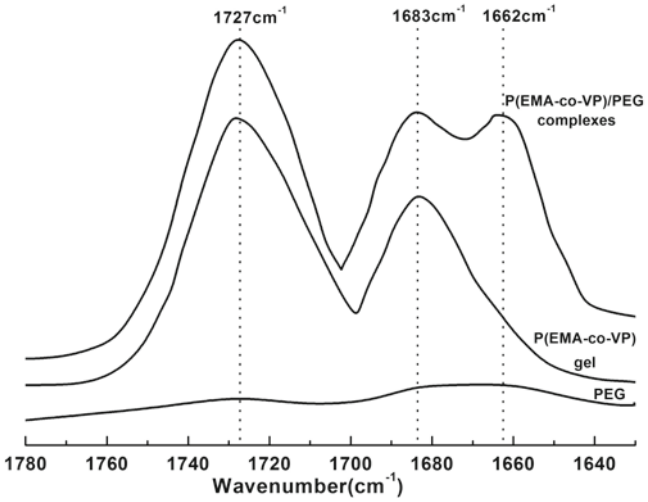

Figure 1. FTIR spectra of P(EMA-co-VP) gel, PEG1000 and P(EMA-co-VP)/PEG1000 complexes

groups and the latter was assigned to hydrogen-bonded carbonyl groups. It is noteworthy that the frequency of C=O stretching of the PEMA does not change, indicating that the carbonyl group of PEMA may not take part in the formation of hydrogen bond, which maybe ascribe to the steric hinderance of $-OCH_2CH_3$. It can reasonable to conclude that the hydrogen bonds mainly exit in between the PEG hydroxyl group and the carbonyl group of PVP.

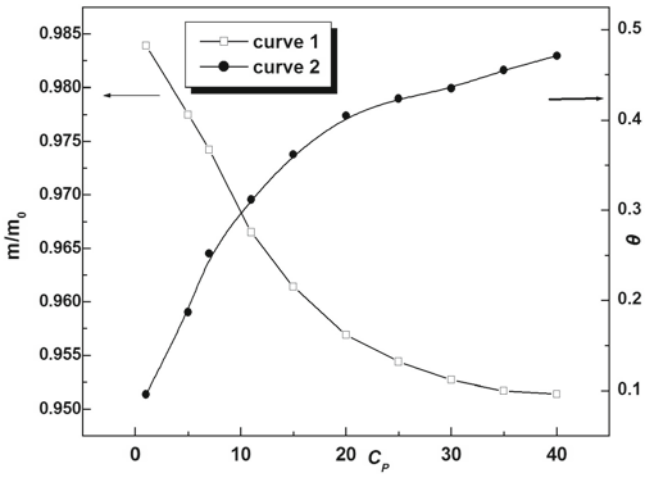

Figure 2. Dependence of the relative mass m/m_0 (curve 1) and binding degree θ (curve 2) of the P(EMA-co-VP)/PEG complexes A series on the initial concentration of PEG (C_P)

Addition of poly(methacrylic acid) (PMAA) or poly-(acrylic acid) (PAA) gels to PEG aqueous solution leads to a sharp shrinkage of the gel volume, and the relative mass of the gel is lowered by a factor of 1.5–3.0[26]; the same phenomenon was reported in the PVP system[27]. Those are called polymer gel collapse. It is to be noted that the transition of weakly cross-linked PMAA or PAA gel from a swollen to the collapsed state is observed at low concentrations of PVP solutions (<5 wt %). However, a slight contraction of gel can be observed for P(EMA-co-VP) gels. Figure 2 (curve 1) illustrates the dependence of the relative mass of the P(EMA-co-VP)/PEG complexes on the initial concentration of PEG (C_P). The increase of C_P up to 35 wt.% leads to a further contraction of the P(EMA-co-VP) gel. Then, in the large region of PEG concentration (35–40 wt.%), the relative mass of the gel changes insignificantly. The contraction of the gels takes place as a result of the formation of an inter-macromolecular gel-polymer complex on the base of hydrogen bonding. P(EMA-co-VP) gels have some hydrophobic properties compared with PAA gels because it has EMA component in its backbone chain. For P(EMA-co-VP)/PEG complexes, EMA units are able to participate in interactions between their hydrophobic group and the main chain of PEG as well as participating in hydrogen bonding, which is the main interacting force. Thus, the cooperativity on complexation is larger and the complexes with PEG are more stable. Figure 2 (curve 2) illustrates the dependence of the binding degree (θ) on initial concentration of PEG. With increasing C_P of PEG solution, the θ value increased simultaneously. This gives the explanation for the conformational changes of P(EMA-co-VP) gel.

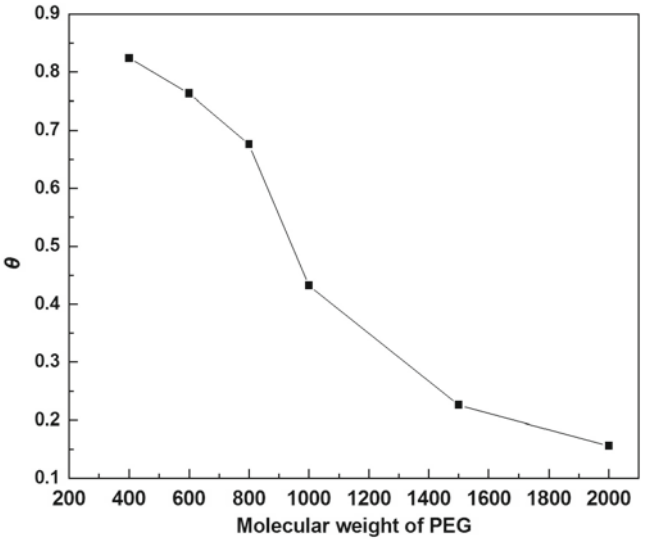

Figure 3. Dependence of the binding degree θ of the P(EMA--co-VP)/PEG complex B series on molecular weight of PEG

The influence of the chain length of PEG on the complexaion with P(EMA-co-VP) gel is obvious, and it should be remembered here that PEG with molecular weight more than 2000 shows to be immiscible with PVP[15–18]. Figure 3 shows the dependence of θ of B series complexes on molecular weight of PEG. θ value gradually decreased with an increase in PEG molecular weight, and the lower the molecular weight of PEG, the easier the complexing of PEG with P(EMA-co-VP) gel. Because the molecular weight of PEG is smaller, the volume fraction the PEG terminal hydroxyl groups is bigger, which contributes to the formation of hydrogen bonds between PEG and P(EMA-co-VP) gel. The above results indicate that PEG with molecular weight no more than 2000 interacts with the P(EMA-co-VP) gel, forming a stable complex. When molecular weight was increased above 2000, the decreasing θ values could be attributed to the steric hindrance from the relatively small mesh size of the polymer network for the long PEG chain to interact with PVP, as evidenced by the late experiments that higher cross-linking density (corresponding to smaller mesh size) of P(EMA-co-VP) networks would hinder the PVP from forming complex with PEG.

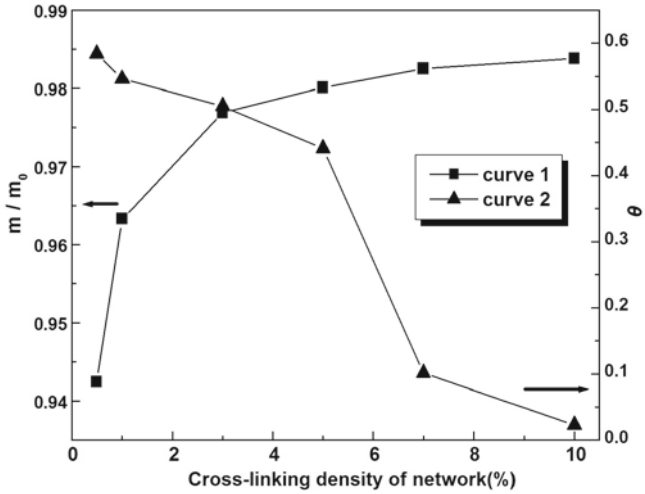

Figure 4. Dependence of the relative mass m/m0 (curve 1) and binding degree θ (curve 2) of the P(EMA-co-VP)/PEG complexes C series on the cross-linking density of network

The degree of cross-linking density is one of the principal factors influencing polymer-polymer complexation[28, 29]. Figures 4 (curve 1) show the swelling behaviors of P(EMA-co-VP) gels with various cross-linking densities, which is a function of PEG concentration in the external solution. It can be seen that the relative mass of the complex increased with increasing the cross-linking density of network. The complex is formed by the interaction between PVP and PEG inside the three-dimensional gel network. An increase in the cross-linking density of the network for PEG with a fixed chain length or in the PEG chain length for a network with a fixed mesh size could prevent PEG molecules from forming complexes inside the P(EMA-co-VP) gel network. The higher the cross-linking density of the network, the harder the complexing of PEG with P(EMA-co-VP) gel, which causes a slight contraction of the gel and an increase of the relative mass of the complex. The decrease of the binding degree with an increase in the cross-linking density of the gel can be explained by the lower swelling degree of the gel due to the higher cross-linking degree of gel which leads to a smaller amount of PEG solution absorbed. Meanwhile, the interpolymer complex formed by a network with a small mesh size must have first developed on the surface layer[30]. This will prevent further interactions of the segments not involved in the complexation process. The above reasons explain that the θ value sharply decreases with increasing cross-linking density of the network as shown in Figures 4 (curve 2).

It is well known that PEG is a semicrystalline polymer with higher crystallinity. However, in P(EMA-co-VP)/PEG complexes, the sample is optically transparent at room temperature, indicating P(EMA-co-VP)/PEG complexes are homogeneous. Figures 5 shows TEM and XRD patterns of two samples, PEG with a molecular weight of 1000 and P(EMA-co-VP)/PEG complexes. 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 5(a) and typical crystal diffraction pattern by TEM observations, corresponding to regular lattice structure, as shown in Figure 5(b).

However, when the crystal PEG complexes with P(EMA-co-VP) gel, its spherulitic structure disappears, as shown in Figure 5(c). A broad, low-intensity peak is observed centered around 16°, suggesting that crystal PEG turns into completely amorphous and P(EMA-co-VP)/PEG complexes are fully miscible with a homogeneous amorphous phase. In other words, the crystal structure of PEG has been changed by the complexation. In Figure 5(d), P(EMA-co-VP)/PEG complexes shows an amorphous halo, indicating that the PEG molecules were dispersed in the amorphous phase and the characteristic of PEG crystal disappears; the P(EMA-co-VP)/PEG complexes are completely miscible. This is in agreement with the visual observations. This is because the hydrogen bonds existed between PVP and PEG are in favour of dispersion of PEG in P(EMA-co-VP) gel and can destroy the structure of PEG crystal aggregates; so, P(EMA-co-VP)/PEG complexes exhibit homogeneous amorphous phase.

A simple and useful method to analyse the complex of PEG with P(EMA-co-VP) gel is the determination of their glass transition temperature (T_g) using DSC. The thermograms of the A series are shown in Fig. 6. T_gs (°C) of the B series and C series are summarized in Table 2. Only one transition is observed for all P(EMA-co-VP)/PEG complexes; a single compositionally dependent glass transition is an indication of full miscibility at a dimensional scale between 20 and 40 nm[31].

The influence of the PEG solution content on P(EMA-co-VP)/PEG complexes have also been studied. As shown in Fig. 6(A), pure PEG1000 only shows the melting temperature without T_g because PEG is easily crystallized and the content of the amorphous phase is very low, and it is very difficult to measure the T_g of PEG in general. In Figure 6(B), the P(EMA-co-VP) gel exhibits one T_g at ca. 67°C and the P(EMA-co-VP)/PEG complexes display a single T_g. However, endothermic peaks due to the melting of PEG crystallites are not observed. These facts mean the crystalline phase of PEG1000 is destroyed in the complex and there is only the amorphous phase in P(EMA-co-VP)/PEG complexes where the segments are molecularly mixed, in agreement with TEM analysis. In the case of T_g of the complexes, it decreases with increasing of PEG solution content. This is because the θ value increased simultaneously with increasing C_P of PEG solution, which leads to more PEG molecular

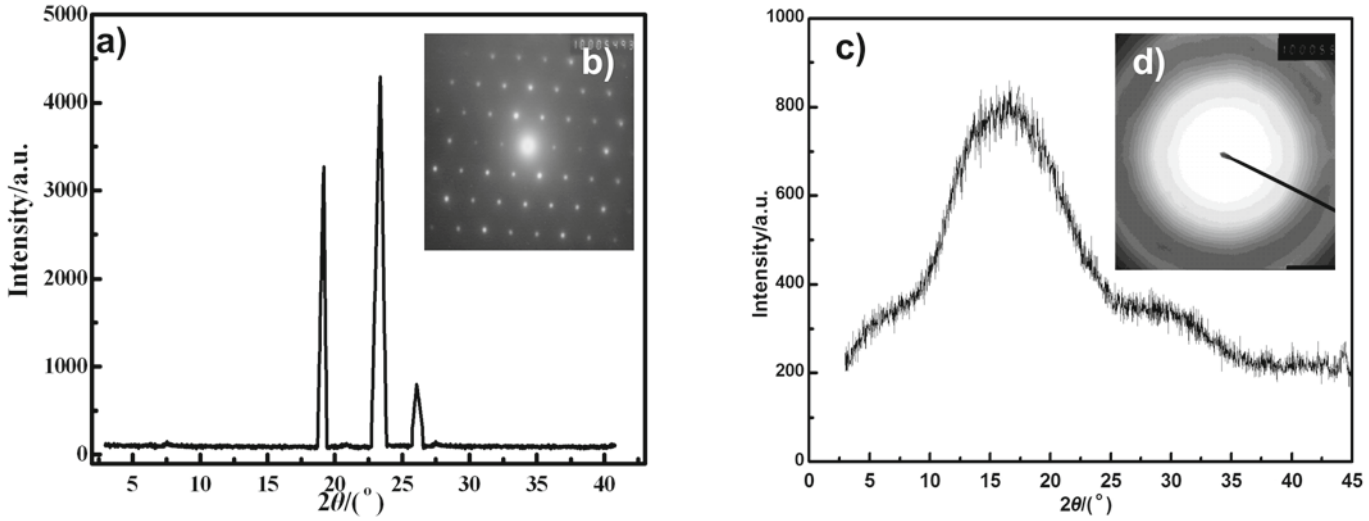

Figure 5. TEM diffraction photographs and XRD pattern for: a), b) PEG1000 homopolymer; c), d) P(EMA-co-VP)/PEG1000 complexes

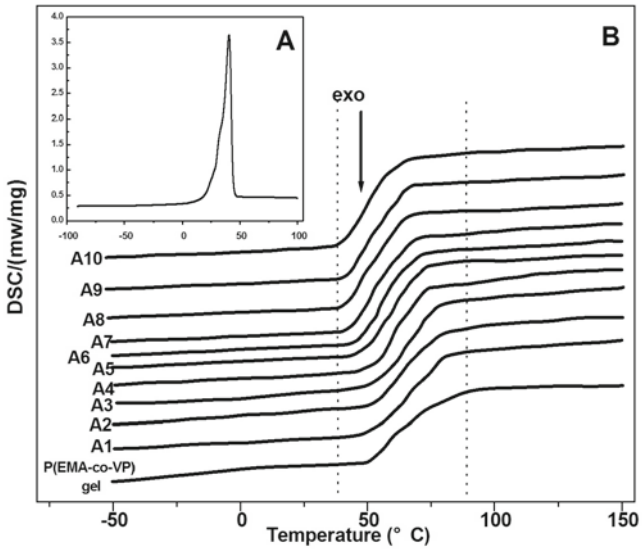

Figure 6. DSC scans of PEG1000 (A), P(EMA-co-VP) gel and P(EMA-co-VP)/PEG complexes A series with various solution content of PEG (B).

complexation with P(EMA-co-VP) gel, thereby causing a decline in T_g of the complexes.

Table 2 indicates the P(EMA-co-VP)/PEG complexes display a single T_g. The complex of PEG with P(EMA-co-VP) gel causes T_g depression of the gel, and it decreases with decreasing of PEG molecular weight; the smaller the molecular weight of PEG, the more the decreased T_g.

The influence of cross-linking density on P(EMA-co-VP)/PEG complexes are presented in Table 2. It is worth noting that cross-linking density plays an important role for T_g of P(EMA-co-VP)/PEG complexes. With increasing of cross-linking density of polymer networks, T_g of P(EMA-co-VP)/PEG complexes shifts to relatively high temperature. It is known that several factors can influence the T_g values of the crosslinked polymers: main chain rigidity, cross-linking density and the chemical structure of the hardener introduced. Relatively high cross-linking densities restrict the motions of polymer chain and make T_g shift to a high temperature region.

CONCLUSIONS

Based on hydrogen bond between the PEG hydroxyl group and the carbonyl group of PVP, P(EMA-co-VP) gel and linear PEG can form complexes, which could be confirmed by FTIR spectra. In P(EMA-co-VP)/PEG complexes, when the molecular weight of PEG is no more than 2000, the complexes are a homogeneous amorphous phase. The molecular weight of PEG, the content of PEG solution and the cross-linking density of P(MMA-co-VP) network have influence on T_g of complexes; with increasing of the molecular weight of PEG and the cross-linking density, the T_g of complexes increases, and decreases with the increasing of the content of PEG solution. However, no excess crystal PEG is observed in the P(EMA-co-VP)/PEG complex, even when C_P reaches 40 wt%.

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Table 2. T_g (°C) of P(EMA-co-VP)/PEG complexes and P(EMA-co-VP) gel

Sample	T_g (°C)	Sample	T_g (°C)	Sample	T_g (°C)	Sample	T_g (°C)
A1	66	A7	54	B3	54	C3	52
A2	65	A8	52	B4	56	C4	54
A3	64	A9	51	B5	57	C5	58
A4	61	A10	50	B6	59	P(EMA-co-VP)	67
A5	59	B1	49	C1	49		
A6	56	B2	51	C2	50		

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