

POLYMER NETWORK-POLY(ETHYLENE GLYCOL) COMPLEXES WITH SHAPE MEMORY EFFECT

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Abstract The complexes of poly(methacrylic acid-co-methyl methacrylate) network with poly(ethylene glycol) stabilized by hydrogen bonds were prepared. By introducing the poly(ethylene glycol), a large difference in storage modulus below and above the glass transition temperature occurred and the complexes exhibited shape memory behaviors. The morphology of complexes was studied by using DSC, WAXD, and DMA. The results indicate that the fixed phase of this kind of novel shape memory materials is the network, and the reversible phase is the amorphous state of PEG:PMAA complex phase. The shape recoverability almost reaches 100%. This type of complexes can be regarded as a novel shape memory network.

Key words Hydrogen bonded complex, Shape memory effect, Storage modulus ratio

INTRODUCTION

Polymer complexes are macromolecular structures formed by the noncovalent association of polymers with the affinity for one another. The major classes of polymer complexes are stereocomplexes, polyelectrolyte complexes, and hydrogen bonded complexes^[1]. Among these complexes, the hydrogen bonded poly(methacrylic acid) (PMAA) network-poly(ethylene glycol) (PEG) complexes have attracted the attention of many researchers due to their special character over the past two decades^[2]. However, research work on the mechanical properties of PMAA-PEG complexes has not been presented.

As is well known, polymer networks generally could not show a satisfactory shape memory behavior, since a large difference in modulus below and above the glass transition temperature and sharp glass-rubber transitions can not be obtained for network. A reasonable way to produce shape-memorized networks is the preparation of networks containing crystallizable polymer chains^[3–6]. In our previous paper^[6], we discovered the shape memory effects of poly(acrylic acid-co-methyl methacrylate)-cetyltrimethylammonium bromide complexes. The shape memory principle of this complex is based on a reversible ordered-disorder transition due to the formation of crystalline aggregates among the long alkyl chains of cetyltrimethylammonium in the complex. All these networks can exhibit shape memory behaviors because their melting transition is sharper and the difference in modulus below and above the melting transition temperature is large enough.

We report here another type of shape memory interpolymer complexes stabilized by hydrogen bonds though crystalline aggregates in this complex cannot be found. The complexes form between chemically crosslinked copolymer of methacrylic acid (MAA) with methyl methacrylate (MMA) (P(MAA-co-MMA)) acting as a proton-donating polymer and poly(ethylene glycol) (PEG) acting as a proton acceptor. By introducing the PMMA component, a softening effect can be expected for the complexes (Kim *et al.* showed that the glass transition

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temperature T_g of the PEG:PAA complex is 180°C)^[7]. We have found that the complex exhibits shape memory effects due to a high elasticity ratio of the glass state modulus (E_g) to the rubbery modulus (E_r) and the ratio of recovery almost reaches 100%. In this paper, the structure and morphology of the complex are briefly characterized and the mechanism of shape memory behaviors with temperature preliminarily discussed.

EXPERIMENTAL

Materials

Methacrylic acid (MAA), methyl methacrylate (MMA), 2,2'-azobis(isobutyronitrile) (AIBN) and N,N' -methylenebis(acrylamide) (MBAA) were commercially available. MAA and MMA were distilled under reduced pressure before use. AIBN, used as a radical initiator, was recrystallized from ethanol solution. MBAA used as a cross-linker, and poly(ethylene glycol) (PEG, molecular weight 1000 and 4000) were used without further purification.

Preparation

P(MAA-*co*-MMA) network was prepared by radical copolymerization of 1.0 mol/L MAA with 1.0 mol/L MMA in the presence of 0.01 mol/L AIBN as initiator and 0.02 mol/L MBAA as crosslinker in dimethyl sulfoxide at 60°C for 24 h. After polymerization, the crosslinked P(MAA-*co*-MMA) was immersed in a large amount of ethanol-water mixture for 1 week to remove the monomers and uncrosslinked polymers, then in water for 2 weeks. The sample was divided into two parts. One represented as P(MAA-*co*-MMA) network was still immersed in water. The other part was immersed in different molecular weight PEG solutions with 6.0 wt% at 25°C for 1 week, then immersed in water to remove PEG absorbed on the surface of P(MAA-*co*-MMA)-PEG complex. According to the molecular weight of PEG, the latter samples were represented as P(MAA-*co*-MMA)-PEG complex 1000 and complex 4000. All specimens were dried under vacuum at room temperature for 3 days.

Measurements

FTIR spectra were obtained with a Nicolet 200SXV FTIR spectrometer. The glass transition temperature was measured using a differential scanning calorimeter (Du Pont 9900) within a temperature range of -50°C to 150°C at a heating rate of 10 K/min. The dynamic mechanical analyses were carried out with a Du Pont 983 instrument at a fixed oscillation amplitude of 0.1 mm and under nitrogen gas purging. The specimens were heated from 30°C to 150°C using a heating rate of 5 K/min.

The method of evaluating the shape memory effect of the shape-memory alloy was adopted to investigate that of our specimens. The shape memory effect was examined by a bending test as follows: a flat strip specimen was folded at 100°C and cooled to keep the deformation. Then the deformed sample was heated again at a fixed heating rate of 2 K/min from 10°C to 140°C and the change of the angle θ_f with temperature was recorded. The ratio of the recovery was defined as $\theta_f/180$.

RESULTS AND DISCUSSION

Various studies of the complexation mechanism have been carried out using pH, viscosity and potentiometric measurements^[8]. These studies show that complexation occurs due to the formation of hydrogen bonds between the carboxyl protons of PMAA and the ether group of PEG, and that the hydrophobic interactions between the CH_2 groups of PEG and the CH_3 groups of PMAA stabilize the complex. Figure 1 is the FTIR spectra of P(MAA-*co*-MMA) network before and after complexation with PEG 4000. The intensity of peak $\nu_{\text{-CH}_2}$ at 2955 cm^{-1} of P(MAA-*co*-MMA)-PEG complex was clearly higher than that of P(MAA-*co*-MMA) network. This spectral result resembles the case of poly(acrylic acid-*co*-methyl methacrylate)-cetyltrimethylammonium bromide complex^[6].

The vibrational frequency $\nu_{\text{C=O}}$ of carboxylic acids is also known to be affected by hydrogen bonding. The $\nu_{\text{C=O}}$ of carboxylic acids usually appears at 1750 cm^{-1} for the non-hydrogen bonded monomeric state and shifts to 1700 cm^{-1} for the hydrogen bonded dimeric structure. On the other hand, the $\nu_{\text{C=O}}$ of carboxylic acids in H complex with the ether oxygen of PEG usually appears at 1730 cm^{-1} ^[9]. Thus, the relative intensity of the

absorption at 1730 cm^{-1} and 1700 cm^{-1} may be taken as the ratio of hydrogen bonds of the carboxylic acid:ether complex to those of the dimeric carboxylic acid structure^[10].

In Fig. 1, the $\nu_{\text{C=O}}$ of carboxylic acids appeared at 1700 cm^{-1} rather than 1750 cm^{-1} for P(MAA-co-MMA) network, indicating that the carboxylic acid groups may have a hydrogen bonded dimeric structure. After complexation, the absorption at 1700 cm^{-1} disappeared, and the C=O stretching absorption was only observed at 1730 cm^{-1} , implying that the C=O stretching absorption of PMAA was overlapped with the C=O stretching absorption of PMMA. This suggests that complexation occurs due to the formation of hydrogen bonds between the PMMA carboxylic protons and the PEG ether group. The conclusion was confirmed by a new absorption at 1110 cm^{-1} ascribed to the C—O—C absorption stretching of PEG.

The thermograms of P(MAA-co-MMA) network, P(MAA-co-MMA)-PEG complex 1000 and the P(MAA-co-MMA)-PEG complex 4000 are shown in Fig. 2. A glass transition temperature at 100°C attributed to the PMAA segment was obtained for both the polymer network and complex 1000. Meanwhile, a melting point at 15°C and a crystalline point at -30°C were found in complex 1000, indicating that a fair amount of PEG 1000 is not complexed with PMAA. This is because the chain length of PEG 1000 is insufficient for the cooperative complexation^[11]. However, endothermic peaks at 50°C due to the melting of PEG 4000 crystallites cannot be observed for complex 4000, and only one glass transition was exhibited at 75°C . These facts mean that the crystalline phase of PEG 4000 is destroyed in the complex and there is only the PEG:PMAA complex phase in complex 4000 where the segments are molecularly mixed. This result was confirmed by wide-angle X-ray measurements (WAXD). The dynamic mechanical analysis result that will be discussed later also suggests that the PEG:PMAA complex phase is amorphous due to a single glass transition. We assume the complexes to be homogeneous to a few hundred angstroms and that motional heterogeneity does not exist in the complexes.

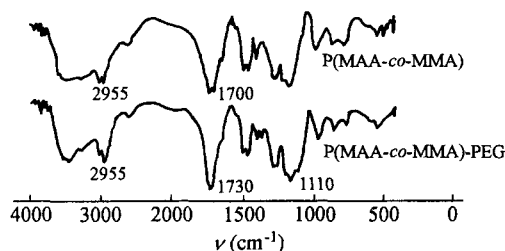


Fig. 1 FTIR spectra of P(MAA-co-MMA) network and P(MAA-co-MMA)-PEG complex 4000

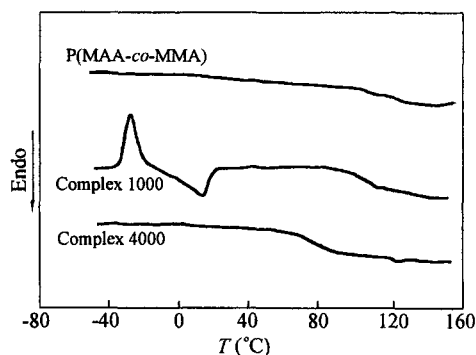


Fig. 2 DSC thermograms of P(MAA-co-MMA) network, complex 1000 and complex 4000

A high elasticity ratio (E_g/E_r), preferably a difference of two orders of magnitude, allows easy shaping at $T > T_s$ (shape memory temperature) and great resistance to deformation at $T < T_s$ ^[12]. One or two of these requirements can be satisfied easily with many of the existing polymeric materials. However, glass transitions are generally not preferred because the transition is not sharp for polymer networks.

The storage modulus E' of the P(MAA-co-MMA) network and P(MAA-co-MMA)-PEG complex 4000 as a function of temperature is shown in Fig. 3 (complex 1000 behaves like a soft elastomer even in the dry state and could not provide its DMA result). A clear decrease in E' for complex 4000 occurred in a temperature range of $50\text{--}90^\circ\text{C}$ and E' values above 90°C became as low as 10^7 Pa which was approximately 2 orders magnitude less than the values below the T_g . However, E' values for P(MAA-co-MMA) network gradually decrease during the glass transition and only a small difference of E_g/E_r was discovered. The storage modulus ratio (defined was $E'_{T_g-20^\circ\text{C}} / E'_{T_g+20^\circ\text{C}}$) of P(MAA-co-MMA)-PEG complex was 44.3, while that of P(MAA-co-MMA) network was only 3.8. A large difference in modulus below and above the transition temperature is the most substantial property underlying the materials shape memory function. With a large elastic modulus ratio (E_g/E_r), high

temperature deformation becomes easy while keeping the resistance to low temperature deformation great. Thus, the P(MAA-co-MMA)-PEG complex shows shape memory effects due to this high modulus ratio. We assume the different dynamic mechanical properties between P(MAA-co-MMA) network and P(MAA-co-MMA)-PEG complex could be interpreted in terms of cooperative inter-polymer hydrogen bonds which alter the dynamics and structures of the component polymers.

Shape memory materials have two phase structures, namely, the fixing phase remembers the initial shape and the reversible phase shows a reversible soft and rigid transition with respect to temperature^[13]. Considering the P(MAA-co-MMA)-PEG complex, the fixing phase is the P(MAA-co-MMA) network, while the reversible phase is the PEG: PMAA complex phase.

Figure 4 shows the $\tan\delta$ -temperature curves of P(MAA-co-MMA) network and P(MAA-co-MMA)-PEG 4000 complex. The $\tan\delta$ of complex reached its maximum at 80°C corresponding to the T_g of complex, while the maximum of $\tan\delta$ for network appeared at 93°C and is significantly lower. Since $\tan\delta$ corresponds to the strain energy dissipated by viscous friction, a large $\tan\delta$ implies that the material is more likely viscous than elastic.

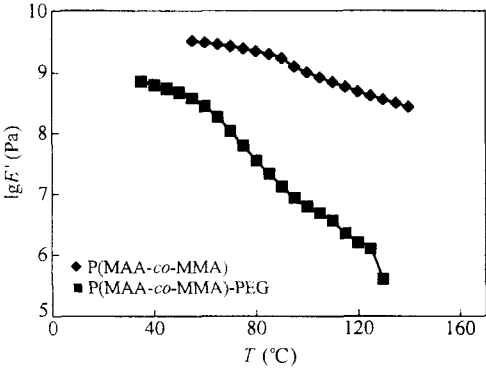


Fig. 3 Temperature dependence of tensile storage modulus E' for P(MAA-co-MMA) network and P(MAA-co-MMA)-PEG complex 4000

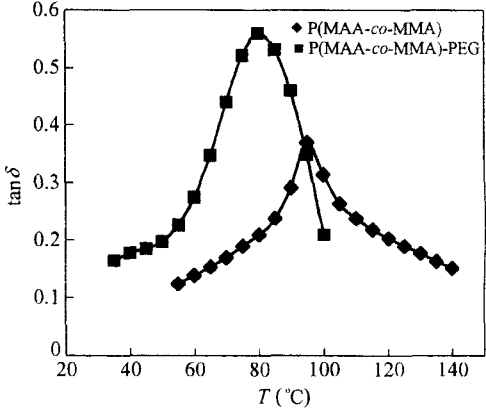


Fig. 4 Plot of $\tan\delta$ versus temperature for P(MAA-co-MMA) network and P(MAA-co-MMA)-PEG complex 4000

The shape memory effect of P(MAA-co-MMA)-PEG complex 4000 and P(MAA-co-MMA) network is demonstrated in Fig. 5. The deformed complex could be recovered rapidly when it is heated again to high temperature. The recoverability could almost reach 100%. But the network shows a slow recovery rate, and it still has some residual deformation that could not be recovered under the conditions of the testing process.

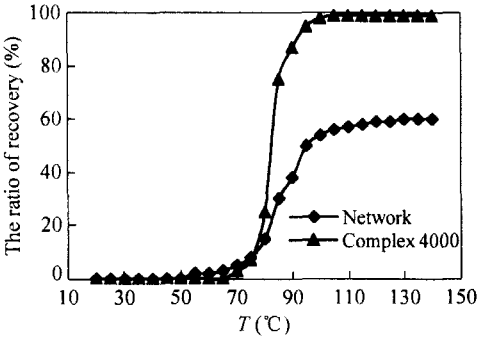


Fig. 5 Shape memory effect of complex 4000 and network

Figure 6 shows the shape memory phenomenon of P(MAA-co-MMA)-PEG complex 4000. The spring shape

sample was heated to 90°C and deformed to a string shape and then cooled to room temperature. The string was rigid and retained its shape. On heating the string again to 90°C, it became soft and returned to its original spring shape. This interesting phenomenon is reversible and cyclically reproducible by repeated temperature changes.

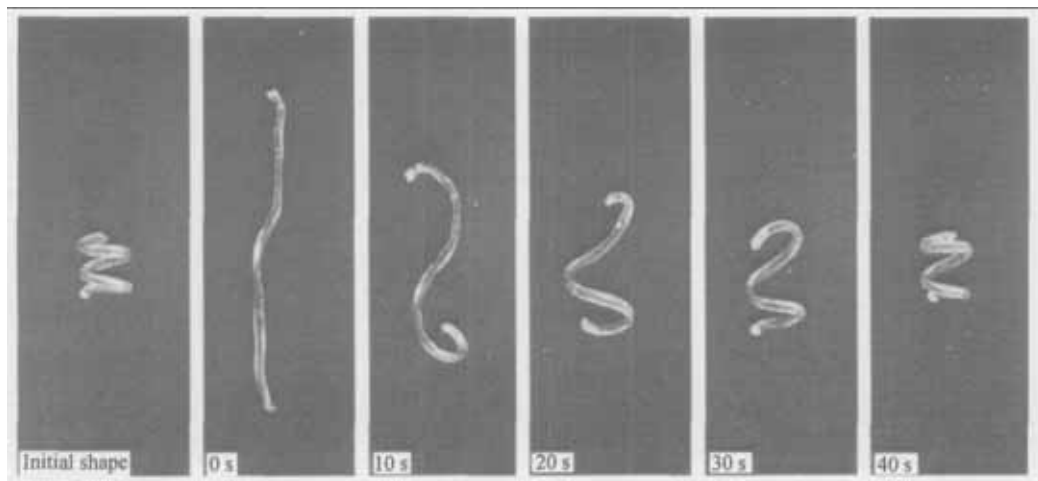


Fig. 6 Shape memory phenomenon of P(MAA-co-MMA)-PEG complex 4000

The initial spring shape sample was heated to 90°C and deformed as a string shape, then cooled to room temperature under constrained conditions. After withdrawal of the external force, the strip shape sample was put in a glass container kept at a constant temperature of 90°C. The photos were taken by a digital camera every 2 s.

CONCLUSION

The morphology of P(MAA-co-MMA)-PEG complex was studied by DSC, WAXD, and DMA. The results indicate that the fixed phase of this kind of novel shape memory materials is the network, and the reversible phase is the amorphous state of PEG:PMAA complex phase. The complexes show shape memory properties due to a large difference in storage modulus below and above the glass transition temperature.

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REFERENCES

- 1 Lowman, A.M., Cowans, B.A. and Peppas, A., *J. Polym. Sci., Polym. Phys. Ed.*, 2000, 38: 2823
- 2 Miyoshi, T., Takegoshi, K. and Terao, T., *Macromolecules*, 1999, 32: 8914
- 3 Osada, Y. and Matsuda, A., *Nature*, 1995, 376: 219
- 4 Kagami, Y., Gong, J.P. and Osada, Y., *Macromol. Rapid Commun.*, 1996, 17: 539
- 5 Reyntjens, W.G., Du Prez, F.E. and Goethals, E.J., *Macromol. Rapid Commun.*, 1999, 20: 251
- 6 Guan, Y., Cao, Y.P., Peng, Y.X., Xu, J. and Albert Chen, S.C., *Chem. Commun.*, 2001, 17: 1694
- 7 Kim, H.J. and Tonami, H., *Kobunshi Ronbunshuu*, 1978, 35: 395
- 8 Miyoshi, T., Takegoshi, K. and Hikichi, K., *Polymer*, 1996, 37: 11
- 9 Philippova, O.E., Karibyants, N.S. and Starodubtzev, S.G., *Macromolecules*, 1994, 27: 2398
- 10 Nishi, S. and Kotaka, T., *Macromolecules*, 1985, 18: 1519
- 11 Osada, Y., *J. Polym. Sci., Polym. Phys. Ed.*, 1980, 18: 281
- 12 Kim, B.K. and Lee, S.Y., *Polymer*, 1996, 37: 5781
- 13 Xu, M. and Li, F.K., *Chinese J. Polym. Sci.*, 1999, 17(3): 203