GUOQIN LIU[1),*)], DELONG XIE[1)], YONG LI[2)], YUXING ZHANG[2)], FANG HUANG[1)]

Shape memory properties of poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate)/poly(ethylene glycol) complexes

RAPID COMMUNICATION

Summary — Poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) [P(MMA-*co*-HEMA)] networks and linear poly(ethylene glycol) (PEG) can form complexes, which show shape memory properties due to a large difference in storage modulus (E') below and above its glass transition temperature (T_g). The morphology of prepared samples was analyzed using transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis. Differential scanning calorimetry (DSC) was used to investigate the thermal properties and dynamic mechanical analysis (DMA) to determine the effect of temperature on the mechanical properties. It was found that the shape recovery ratio could reach 98 %.

Keywords: poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate), poly(ethylene glycol), glass transition temperature, shape memory properties.

PAMIĘĆ KSZTAŁTU KOMPLEKSÓW POLI(METAKRYLAN METYLU-*co*-METAKRYLAN 2-HYDROKSYETYLU)/POLI(GLIKOL ETYLENOWY)

Streszczenie — W matrycę, którą był poli(metakrylan metylu-*co*-metakrylan 2-hydroksyetylu) [P(MMA-*co*-HEMA)] wbudowano liniowy poli(glikol etylenowy) (PEG) w ilości 10—20 % mas. Próbka tak utworzonego kompleksu, ze względu na dużą różnicę składowej rzeczywistej modułu zespolonego (E') charakteryzującej materiał w temperaturze niższej i wyższej od temperatury zeszklenia (T_g), wykazywała zdolność do zapamiętania nadanego kształtu (rys. 4). Otrzymane próbki poddano badaniom morfologicznym za pomocą transmisyjnej mikroskopii elektronowej (TEM) i dyfrakcji rentgenowskiej (XRD) (rys. 1 i 2). Użyto również różnicowej kalorymetrii skaningowej (DSC) do zbadania właściwości termicznych (rys. 3) oraz dynamicznej analizy mechanicznej (DMA) w celu określenia wpływu temperatury na właściwości mechaniczne (rys. 5). Stwierdzono, że wskaźnik odzyskiwania kształtu może osiągać 98 %.

Słowa kluczowe: poli(metakrylan metylu-*co*-metakrylan 2-hydroksyetylu), poli(glikol etylenowy), temperatura zeszklenia, pamięć kształtu.

There is no doubt that shape memory alloys have attracted wide attention all the time. However, shape memory polymers by far surpass metallic shape memory alloys in their shape memory properties [1], which can response to changes in the external conditions such as ionic strength, pH, temperature and so on [2—5]. These characteristics make them desirable for a multitude of applications, including drug-delivery systems, biocatalysts, biosensors, *etc.* [6—8]. Thermally induced shape memory polymers are those that have the capability of changing their shapes from a temporary shape to a permanent shape above and below their switching transition temperature (T_{trans}) [1, 9]. Normally T_{trans} can either be the glass transition (T_g) or the melting temperature (T_m) of a polymer. They can be designed as polymer networks, including covalently crosslinked and physically crosslinked amorphous or crystalline copolymers, as well as polymer blends [10—14], which consist of two segments: the switching one with T_{trans} for the fixation of temporary shape and the hard one for the fixation of the permanent shape [1, 15].

2-Hydroxyethyl methacrylate (HEMA) is a synthetic comonomer, which is very toxic for the living cells. However, in its polymerized form as poly(2-hydroxyethyl methacrylate) (PHEMA), it is a highly compatible polymer with the living tissues [16, 17].

In the present study, we have developed a shape memory polymer based on methyl methacrylate (MMA)

[1)] Henan University of Technology, College of Material Science and Engineering, Zhengzhou, 450001, China.

[2)] North China University of Water Conservancy and Electric Power, School of Mechanical Engineering, Zhengzhou, 450045, China.

[*)] Corresponding author; e-mail: liugq1970@126.com

and HEMA as synthetic comonomers, and poly(ethylene glycol) (PEG), namely P(MMA-*co*-HEMA)/PEG complexes, which could be used as a material for biomedical applications. The novelty of this work is the choice of HEMA for generating new types of shape memory polymers. To the best of our knowledge, HEMA has not been used yet as a comonomer for shape memory polymers. Crystalline aggregates can not be found by X-ray diffraction (XRD), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC) analysis, although PEG is a semicrystalline polymer.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), 2,2′-azobis(isobutyronitrile) (AIBN) and ethylene glycol dimethacrylate (EGDMA) of analytical grade were obtained from Aldrich Chemical Co. MMA was distilled under reduced pressure before use. AIBN, used as a radical initiator, was recrystallized from ethanol solution. HEMA was used as received and EGDMA was used as a crosslinker without further purification.

Poly(ethylene glycol) (PEG) (Aldrich) with catalogue number-average molecular weight of $\overline{M}_n$ = 2000 was dried by heating at 60 °C for 8 h under vacuum.

Preparation of complexes

P(MMA-*co*-HEMA)/PEG complexes were prepared by radical copolymerization of 58.5 wt. % of MMA and 15 wt. % of HEMA in the presence of 0.5 wt. % of AIBN as an initiator, 6 wt. % of EGDMA as a crosslinker and 20 wt. % of linear PEG. The reaction mixtures were bubbled with nitrogen for 15 min to remove the oxygen from the mixture and then injected into a cylindrical glass tube with 7 mm in diameter. Copolymerization was carried out at 55 °C for 24 hours. P(MMA-*co*-HEMA)/PEG complexes were quenched and then dried under vacuum at room temperature for 10 days to remove unreacted monomers.

Methods of testing

The thermal analyses were carried out with a differential scanning calorimeter (DSC, DuPont 9900). The spherulites were observed and photographed through a polarizing optical microscope Jiangnan XPR-2 (China) equipped with a digital camera and a heating stage. The dynamic mechanical analyses (DMA) were carried out with a DuPont 983 DMA apparatus at the fixed oscillation amplitude of 0.1 mm and under nitrogen gas purge. The X-ray diffraction (XRD) analysis was performed with a Philips X'pert Pro MPD, using Ni-filtered CuKa radiation. Transmission electron microscopy (TEM) measurements were carried out on a JEM-100CX Microscopy (Japan Electronic Company).

RESULTS AND DISCUSSION

P(MMA-*co*-HEMA)/PEG complexes were prepared by radical copolymerization and crosslinking of MMA with HEMA in the presence of linear PEG. It is well known that PEG is a semicrystalline polymer and well-developed spherulite, with higher crystallinity and the size of about 2000 μm in diameter, as shown in Figure 1a. Spherulites are the basic morphology for polymers crystallized from melting or concentrated solutions, which are high-order crystal structures with spherical textures, composed of lamellar crystallites, shaped like ribbons that radiate from the center, separated by amorphous material [18]. Because of its spherulitic structure, neat PEG ($\overline{M}_n$ = 2000) can show typical crystalline diffraction pattern by TEM, corresponding to regular lattice structure, as shown in Figure 1b and 1c, PEG shows its high and sharp X-ray peaks, and two main diffraction peaks at about 18.6° and 23.4°.

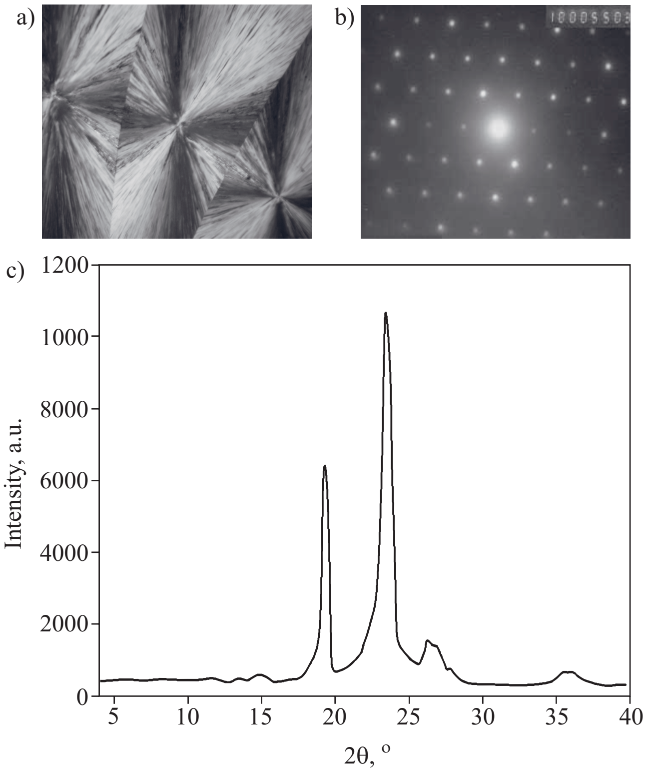

Fig. 1. Optical micrograph (a), TEM diffraction photograph (b) and XRD pattern (c) for neat PEG

On the face of them, P(MMA-*co*-HEMA)/PEG complexes are optically transparent. The PEG spherulitic structure cannot be observed using a polarizing microscope in P(MMA-*co*-HEMA)/PEG complexes, as it is shown in Figure 2a. The P(MMA-*co*-HEMA)/PEG com-

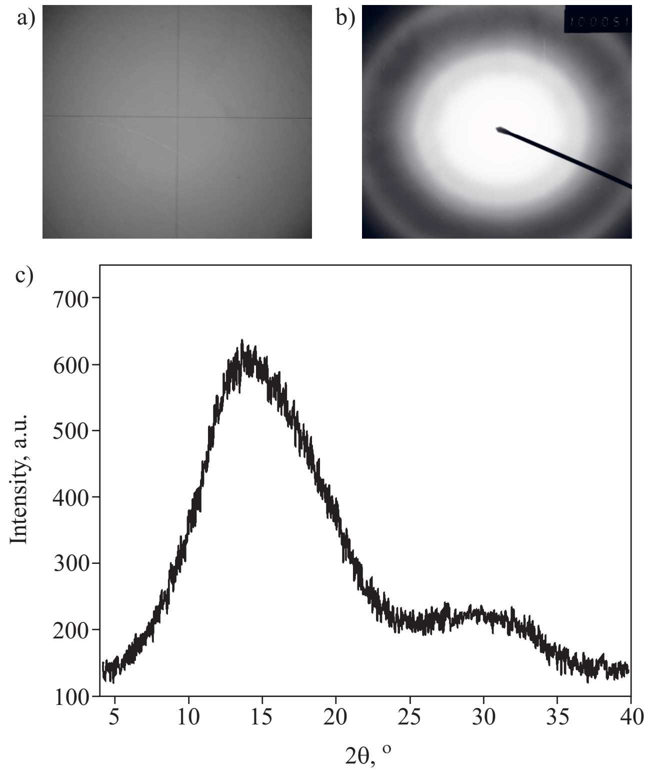

Fig. 2. Optical micrograph (a), TEM diffraction photograph (b) and XRD pattern (c) for P(MMA-co-HEMA)/PEG

plexes obtained by radical copolymerization showed an amorphous halo in Figure 2b. Figure 2c represents the XRD scattering patterns of the P(MMA-*co*-HEMA)/PEG complexes, and, compared to Figure 1c, the sharp X-ray peaks of PEG disappear. A broad, low-intensity peak is observed centered around 14°, suggesting that PEG was fully miscible with P(MMA-*co*-HEMA) networks. P(MMA-*co*-HEMA)/PEG complexes are fully miscible with a homogeneous amorphous phase. In other words, the crystal structure of PEG has been changed by the procedure of blending.

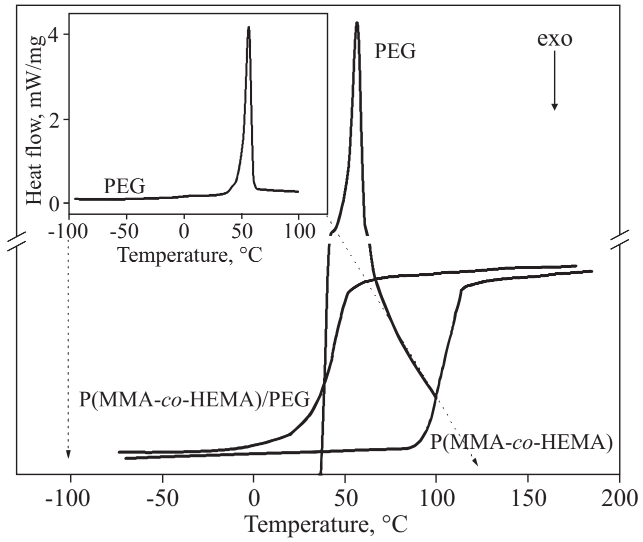

Fig. 3. DSC curves of PEG, P(MMA-co-HEMA) networks and P(MMA-co-HEMA)/PEG complexes

As it is shown in Figure 3, presenting the results of DSC measurements, P(MMA-*co*-HEMA)/PEG complexes show only a single glass transition at $T_g \approx 41$ °C. The endothermic peak of PEG crystallites was not observed for complexes, suggesting that they are fully miscible. The existence of intermolecular forces favors the dispersion of PEG in P(MMA-*co*-HEMA) networks and destroys the structure of PEG crystal aggregates. So, P(MMA-*co*-HEMA)/PEG complexes exhibit the homogeneous amorphous phase. This result coincides with the findings in TEM and XRD observations presented in Figure 2.

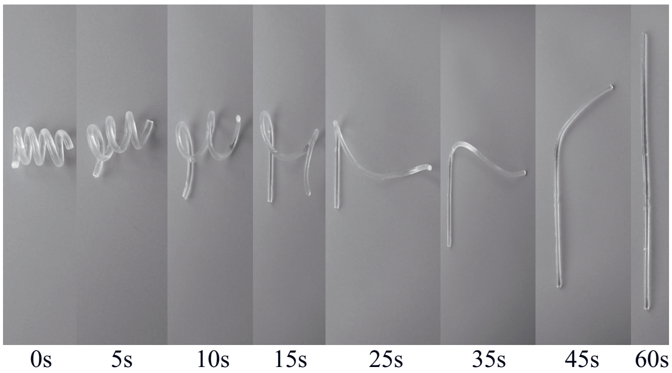

Fig. 4. Transition from the temporary shape (a spiral) to the permanent shape (a rod) at 65 °C

The shape memory properties were found to occur by changing the operation temperature below and above the T_g (*ca.* 41 °C) of the P(MMA-*co*-HEMA)/PEG complexes. The photos presented in Figure 4 show the steps the sample returns to the original rod shape. The complexes behave as a hard plastic at room temperature and its permanent shape is a rod (7 mm in diameter and 100 mm long). When the rod was heated up to 65 °C, it became soft and could easily be deformed to a spiral (temporary shape) under external force. Next, the spiral was cooled down to room temperature and the temporary shape was fixed without loading, the strained state was very stable, even after unloading. However, if the temperature was raised to 65 °C again, the complexes quickly (in 60 s) returned to the initial shape with the shape recovery ratio of above 98 %. This interesting phenomenon is reversible and can be repeated at least 15 times.

The crosslinked P(MMA-*co*-HEMA) networks were designed as the fixed phase, while the amorphous PEG-PHEMA complex phases act as the reversible phase. An excellent shape memory materials should have a shape memory ratio of more than 90 %. Normally, a high elasticity ratio (E_g/E_r, where E_g is the glass state modulus, E_r is the rubbery modulus), preferably as much as two orders of magnitude, is needed to allow the easy shaping at $T > T_g$ and high resistance to deformation at $T < T_g$. On the other hand, a large difference in the modulus below and above the transition temperature is the most significant factor to render P(MMA-*co*-HEMA)/PEG complexes shape memory behavior. With a large elasticity ratio, high temperature deformation becomes easy, while keeping the high resistance to low temperature deformation [19].

P(MMA-*co*-HEMA) does not show the shape memory behavior below 100 °C. By introducing linear PEG in P(MMA-*co*-HEMA), they can form complexes. The addition of PEG to P(MMA-*co*-HEMA) networks not only causes a depression in the T_g and stiffness of P(MMA-*co*-HEMA) networks, but also alters the dynamic mechanical behavior of P(MMA-*co*-HEMA) networks, as it is shown in Figure 5. When the complexes were heated to 65 °C (above T_g + 20 °C), they can transform from the glass state to rubber-elastic state, which makes the complexes flexible and they can be easily deformed under external force. When the complexes were cooled down to the room temperature, they returned to glass state. It can be considered that the P(MMA-*co*-HEMA)/PEG complexes possessed the shape memory effect due to a large difference in storage modulus below and above T_g. Here, the storage modulus ratio (defined as $E'_{Tg\text{-}20\,°C}/E'_{Tg+20\,°C}$) can be more than 270 for P(MMA-*co*-HEMA)/PEG.

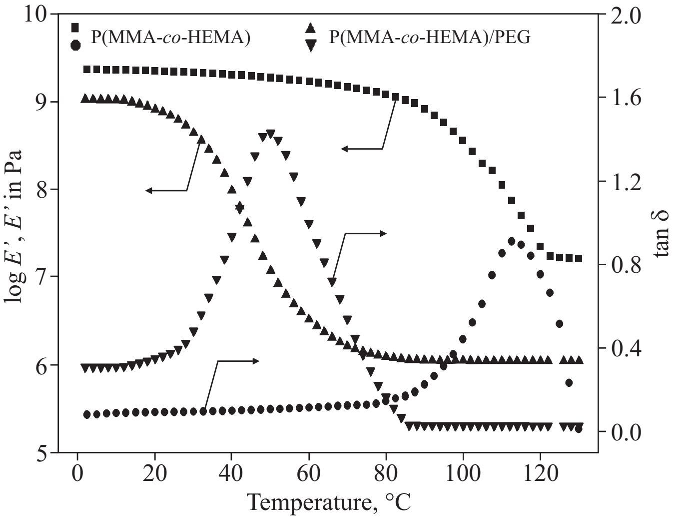

Fig. 5. Storage modulus (E') and loss tangent (tan δ) determined by DMA for P(MMA-co-HEMA)/PEG complexes and P(MMA-co-HEMA) networks

Shape memory polymer generally contains a fixing phase and a reversible phase. The fixing phase imparts the level of rigidity, dimensional stability and thermal resistance, while the reversible phase provides the elastic properties primarily recovery and energy absorption. For the P(MMA-*co*-HEMA)/PEG complexes, the fixing phase was the chemical crosslinked phase, while the reversible phase was the PEG-PHEMA complex phase.

CONCLUSIONS

The P(MMA-*co*-HEMA)/PEG complexes show shape memory properties due to a large difference in storage modulus below and above the glass transition temperature and its recovery ratio can reach 98 %. Although PEG ($\overline{M}_n$ = 2000) is a semicrystalline polymer, crystalline aggregates cannot be found in obtained complexes by XRD, TEM and DSC. These properties of P(MMA-*co*-HEMA)/PEG complexes can be designed, allowing them to be a kind of potential biomaterials for use in medicine and for other applications for materials interacting with biological systems.

REFERENCES

1. Lendlein A., Kelch S.: *Angew. Chem. Int. Ed.* 2002, **41**, 2034.
2. Lendlein A., Langer R.: *Science* 2002, **296**, 1673.
3. Samra B. K., Galaev I. Y., Mattiasson B.: *Angew. Chem. Int. Ed.* 2000, **39**, 2364.
4. Hu Z., Zhang X., Li Y.: *Science* 1995, **269**, 525.
5. Osada Y., Matsuda A.: *Nature* 1995, **376**, 219.
6. Liu C., Qin H., Mather P. T.: *J. Mater. Chem.* 2007, **17**, 1543.
7. Gunes I. S., Cao F., Jana S. C.: *Polymer* 2008, **49**, 2223.
8. Yang B., Huang W. M., Li C., Li L.: *Polymer* 2006, **47**, 1348.
9. Behl M., Lendlein A.: *Mater. Today* 2007, **10**, 20.
10. Rousseau I. A., Mather P. T.: *J. Am. Chem. Soc.* 2003, **125**, 15 300.
11. Liu C., Chun S. B., Mather P. T., Zheng L., Haley E. H., Coughlin E. B.: *Macromolecules* 2002, **35**, 9868.
12. Lendlein A., Schmidt A. M., Langer R.: *PNAS* 2001, **98**, 842.
13. Lee B. S., Chun B. C., Chung Y. C., Sul K. I., Cho J. W.: *Macromolecules* 2001, **34**, 6431.
14. Liu C., Mather P. T.: Proceedings of the annual technical conference — society of plastics engineers, 61st, vol. 2. Brookfield, CT, USA: Society of Plastics Engineers 2003, pp. 1962—1966.
15. Behl M., Bellin I., Kelch S., Wagermaier W., Lendlein A.: *Adv. Funct. Mater.* 2009, **19**, 102.
16. Grodzinski J. J.: *Polym. Adv. Technol.* 2010, **21**, 27.
17. Tomić S. L., Mićić M. M., Dobić S. N., Filipović J. M., Suljovrujić E. M.: *Radiat. Phys. Chem.* 2010, **79**, 643.
18. Keller A.: *J. Polym. Sci.* 1959, **39**, 151.
19. Kim B. K., Lee S. Y., Xu M.: *Polymer* 1996, **37**, 5781.

Received 7 I 2013.