

Shape memory characterization of polytetra methylene oxide/poly (acrylic acid-co-acrylonitrile) complexed gel

J. Dyana Merline · C. P. Reghunadhan Nair ·
C. Gouri · T. Shrisudha · K. N. Ninan

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Abstract Polymer gels of poly(acrylic acid-co-acrylonitrile) [p(AA-co-AN)] of varying compositions were synthesized and complexed with polytetramethylene oxide (PTMO) to get PTMO/p(AA-co-AN) complexed gels. The complexation occurred through H-bonding of carboxyl group of acrylic acid with ether group of PTMO. The PTMO/p(AA-co-AN) gels were characterized by DSC, DMTA and swelling ratio. Their shape memory property was evaluated by bending tests. The swelling ratio of [p(AA-co-AN)] in PTMO (as solvent) increased and T_g of the complexed gel diminished with enhancement in the acrylic acid-content in the copolymer. The modulus ratio (E_g/E_r) increased with the acrylic acid content, which is conducive to better shape memory and shape recovery properties of the gels. The influence of the copolymer composition on the swelling ratio, T_g , dynamic mechanical and the shape memory properties of the complexes is examined and presented. The gels showed a shape recovery of >90%, which increased with the acrylic acid content in the copolymer.

Introduction

Shape memory polymers (SMPs) are typically temperature sensitive functional polymers that basically consist of two phases; a fixed phase and a reversible phase with diverging

phase transitions [1]. The fixed phase could arise from the entanglement of polymeric chain or the chemical or physical cross-linked points and the reversible phase (or the switching phase) is constituted by physical phenomenon like crystallization, H-bonding etc of the polymer segments. In the thermo-responsive SMP, the reversible phase is softened by heating. When the shape memory polymer is deformed at a temperature above T_g and suddenly cooled to a temperature below T_g , the deformed shape becomes frozen. When the frozen polymer is heated above T_g , the polymer recovers its original shape [2]. SMP materials have the ability to recover large strains imposed by mechanical loading. They are designed to have a large change in elastic modulus above and below the glass transition temperature (T_g) of the amorphous phase [3]. Large difference in elastic modulus leads to better and faster shape recovery properties. Shape memory gels are one of the important classes of SMPs that have evinced current interest because of their effective response to external stimuli such as solvent, pH, electric fields and light [4]. Many thermo-sensitive polymers such as poly(N-substituted acryl amide) [5], poly(N-alkyl amide) [6, 7], polyvinyl ether [8], poly(2-ethyl-2-oxazoline) [9] etc. have been reported. These thermo-sensitive polymers are generally designed by endowing water-soluble polymers with suitable hydrophobicity. Particularly, their volumes can be changed by several orders of magnitude in response to a variety of external stimuli such as solvent, temperature, pH, electric field and light. Such smart gels have been explored to perform various functions including artificial muscles and organs, drug delivery devices, chemical valves and actuators [10–12]. Since stimuli-responsive gels change their structures and physical properties in response to their surrounding environment, they can be widely applied as biomaterials such as controlled drug release and delivery

J. D. Merline · C. P. R. Nair (✉) · C. Gouri ·
T. Shrisudha · K. N. Ninan
Propellants and Special Chemicals Group, PCM Entity,
Vikram Sarabhai Space Centre, Thiruvananthapuram 695022,
India
e-mail: cprnair@gmail.com

systems, on-off switching materials, biosensors and adsorptive materials [13]. Liu et al. [14] studied the shape memory behaviour of H-bonded complex of poly (acrylic acid-co-methylmethacrylate) networks with polyethylene glycol of varying molecular weight. The complexation is achieved through the polycarboxylic acid that can form intermacromolecular complexes with polyethylene glycol through the H-bonding between the carboxyl group of poly (carboxylic acid) and the ether O-atom of polyethylene glycol [15, 16]. In such a copolymer, the possibility of H-bonding between –COOH group and the ester group of methyl methacrylate could reduce the probability of H-bonding with the second polymer, and consequently the extent of complexation.

In the present work, we have examined the poly (acrylic acid-co-acrylonitrile) [p (AA-co-AN)] as the complexing agent for polytetramethylene oxide (PTMO). PTMO was chosen as this polymer is known for imparting good shape memory characteristics to polymer systems [17]. This work is an attempt to synthesise shape memory gels based on polyacrylic-PTMO complexes and correlate their shape memory property to the copolymer structure and gel composition. The copolymer gel of poly(AA-co-AN) was synthesized from acrylic acid (AA) and acrylonitrile (AN) using methylene bisacrylamide (MBA) as cross-linker. AN was selected as it does not form intramolecular H-bond with its comonomer, i.e. AA in the copolymer. The selection of AN was also based on the possibility of achieving higher glass transition temperature for the copolymer, since suitable transition temperature is needed for the broad application of the derived shape memory gels. The complexed gels were characterized for thermal, dynamic mechanical and shape memory properties.

Experimental

Materials

Acrylic acid (AA), acrylonitrile (AN) (SISCO Research Laboratories, Mumbai), methylene bisacrylamide (MBA) (Spectrochem, Mumbai), ammonium persulfate (APS) (Central Drug House, New Delhi), tetraethylene methylene ethylene diamine (TEMED) (Central Drug House, New Delhi), dimethylsulphoxide (DMSO) (Spectrochem, Mumbai) and polytetramethylene oxide (PTMO, $M_n = 2000$) (Aldrich Chemicals, USA) were used to synthesize the polymer gel complexes. AA and AN were distilled before use. PTMO was dried in a rotavapour at 80 °C/5 h before use. MBA, APS, TEMED and DMSO were of analytical grade and were used without further purification.

Polymer synthesis

The copolymer poly(AA-co-AN) was synthesised by free radical copolymerisation of the monomers. For a typical reaction, AA (2.88 g, 0.04 mol), AN (2.12 g, 0.04 mol) were added to 40 mL DMSO containing 2 gm APS in a RB flask. TEMED (8 drops as the accelerator) and MBA (16.1 mg, 0.4 mmol) as cross linker were then added. The reaction mixture was mechanically stirred for 10 min at 25 °C. The reaction mixture was then injected into a cylindrical glass tube of inner diameter 12 mm. Gelation was carried out at room temperature for 24 h. After polymerization, the cross-linked poly(AA-co-AN) gel was immersed in 50/50wt% of ethanol-water solution for two weeks to remove the monomers and noncross-linked polymer. Then, it was immersed in a large amount of distilled water for three weeks until it reached the equilibrium swelling. The poly(AA-co-AN) gel was then dried under vacuum for 10 days at 60 °C. The dried polymers was then immersed in PTMO at 25 °C for one month for complex formation to get PTMO/poly(AA-co-AN) complexed gel. The gel was wiped with a soft tissue to remove excess PTMO and weighed. Then the complexed gels were vacuum dried at 60 °C for 10 days.

Polymer gel characterisation

Differential scanning calorimetry

The thermal properties were measured by a Mettler DSC-20 analyser using aluminium sample pans. The sample size of 5 mg which was stored in dessicator were heated from –50 °C to 125 °C at a heating rate of 5 °C/min.

Swelling ratio

To find the swelling ratio, a known weight of a small piece of vacuum dried poly(AA-co-AN) gel (W_{ds}) was soaked in PTMO (5 gm) for 15 days. The weight of the swollen polymer gel (W_s) was obtained by removing the excess solvent (PTMO) by blotting with filter paper. From W_s and W_{ds} , the swelling ratio (Q) was calculated as

$$Q = W_s/W_{ds}.$$

Dynamic mechanical analysis

Dynamic mechanical properties were determined in Rheometrics Scientific Model Mark IV (UK) analyzer in the tensile mode at a frequency of 1 Hz. The specimens were heated from –100 °C to 150 °C at a heating rate of 5 °C/min. The data of storage modulus and tan delta were recorded.

Shape memory evaluation

The method of evaluating shape memory alloy [16] was adopted for the polymer gels as shown in Fig. 1. A straight rod polymer gel of length 50 mm and diameter 5 mm was used for the tests. The gel was heated to a temperature $T > T_g$ and deformed to an angle (θ_i) and then cooled to fix the deformation. Then the deformed gel was heated to $T > T_g$, the change in angle (θ_f) was recorded. The ratio of recovery was found as $(\theta_i - \theta_f) / \theta_i$. The samples were subjected to bending test for three times and average values are taken.

Results and discussion

Synthesis and formulations of polymer gel complexes

Table 1 compiles the formulations of copolymer gel of poly(AA-co-AN). Different compositions of poly(AA-co-AN) gel were prepared by varying the content of AA and AN monomers while maintaining the molar concentration of cross-linker the same. Table 2 gives the thermal and swelling properties of PTMO/poly(AA-co-AN) gel. While complex formation, the poly(AA-co-AN) gel contracts. The main reason for the contraction of gel is the intermacromolecular complex formation [15] and it was suggested that the driving force for the aggregation of the complex is partly hydrophobic interactions [18]. In PTMO/poly(AA-co-AN) gel the involvement of AA in H-bonding is the main interacting force between the copolymer and PTMO. AN is unlikely to be involved in H-bonding with AA or with PTMO. This is also evident from the fact that the swelling ratio of poly(AA-co-AN) in PTMO decrease with AN content of the copolymer, as this group cannot complex with PTMO through H-bonding. Thus, there

Table 1 Formulations poly(AA-co-AN) gel

poly(AA-co-AN) gel (Sample Reference)	% of AA (mol%)	% of AN (mol%)
G-1	75	25
G-2	50	50
G-3	25	75
G-4	0	100

Table 2 T_g and swelling properties of poly(AA-co-AN) gels in PTMO

PTMO/p(AA-co-AN) gel (Sample Reference)	Swelling ratio	T_g (°C) (from DMA)
PG-1	1.43	45
PG-2	1.41	50
PG-3	1.05	80
PG-4	1.00	110

occurs a strong interaction between the ether O-atom of PTMO and the carboxy group of AA. With increase in swelling ratio, PTMO content increases in the complexed gel and it leads to a better shape memory property. The T_g (which was obtained from DMA) of the PTMO/poly(AA-co-AN) dry gel increases with the AN composition (Table 2). T_g and thereby, the switching temperature can thus be tuned by compositional variation of the precursor copolymer.

Differential scanning calorimetry

Figure 2 shows the thermal profiles of PTMO/poly(AA-co-AN) gel. The glass transition temperature (T_g) of the PTMO/poly(AA-co-AN) gel increased with the AN content. Endothermic peak due to the melting of PTMO crystallites was not observed for the complexes. All the complexed gels showed only a single transition temperature, suggesting that these complexes form a homogeneous

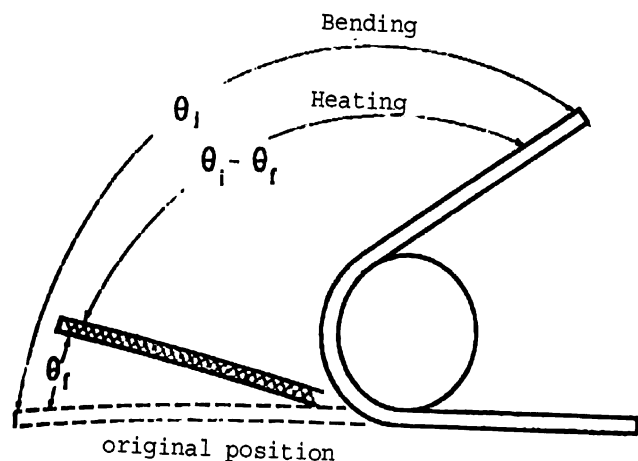


Fig. 1 Schematic representation of bending test

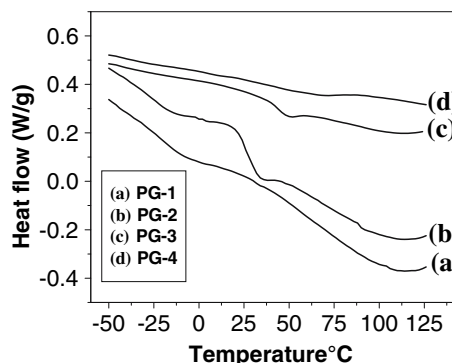


Fig. 2 DSC thermal profiles of PTMO/poly(AA-co-AN) gel, Heating rate: 5 °C/min

amorphous. During the heating process, the molecular chain of PAA–PTMO complex acts as amorphous phase for the transition from the glassy to the rubbery state.

Dynamic mechanical analysis

Figure 3a and b show the DMA of the PTMO/poly(AA-co-AN) gel. The curve shows the variation of storage modulus (E') and $\tan\delta$ with temperature. The DMA profiles were different for the polymer systems. PG-1 and PG-2 showed only a single major transition, while PG-3 manifested two stage transitions at $\sim 25^\circ\text{C}$ and 75°C in the E' curve. These transitions can be attributed to the T_g of polymer segments complexed with PTMO to different extents (AA rich segments and AN rich segments). As the AN content is maximum in PG-3, the complexation is less effective. In this case the modulus initially increased with temperature due to the crystallization of polyacrylonitrile segments. PG-4 did not form complex with PTMO but showed two T_g with a major transition at 110°C . The $\tan\delta$ graphs (Fig. 3b) show the major phase transitions. PG-1 and PG-2 showed only single $\tan\delta$ maxima while PG-3 manifested two $\tan\delta$ maxima at 28°C and 80°C (at 80°C is the major transition). The reported T_g 's (Table 2) corresponds to the respective $\tan\delta$ peak maxima for the major transition. The DSC and DMA profiles are in mutual agreement. Sharp decrease in E' occurred in the region of T_g for all the samples. The modulus ratio (E_g/E_r) (glassy state modulus/rubbery state modulus), which was calculated as ($E'_{T_g+20^\circ\text{C}}/E'_{T_g-20^\circ\text{C}}$) of the PTMO/poly(AA-co-AN) gel increased with the PTMO content, i.e. E_g/E_r ratio increased with the swell ratio. This ratio is normally considered as an index of the shape recovery potential [19]. Figure 4 shows the variation of E_g/E_r ratio of the PTMO/poly(AA-co-AN) gel with the swelling ratio. The composition PG-4, which lacked complexation with PTMO have a E_g/E_r ratio of 10. For rest of the PTMO/poly(AA-co-AN) gels, the E_g/E_r ratio is of 2 orders of magnitude higher which is imperative for better shape memory property. Effectively, PG-4 lacks shape memory property. A large elastic ratio is desirable for better shaping at $T > T_g$ and better material strength at $T < T_g$ [20]. The highest E_g/E_r ratio is observed for PG-1 with highest swell ratio of 1.43. This gel manifested good shape memory property. The $\tan\delta$ value of the PTMO/poly(AA-co-AN) gels increases with the AA-content. The $\tan\delta$ value corresponds to the strain energy dissipated by viscous friction and higher $\tan\delta$ implies the more viscous nature [19]. It was also noted that lowering of T_g was associated with an increase in $\tan\delta$ value. The highest $\tan\delta$ value of 1.4 was observed for PG-1 and PG-2.

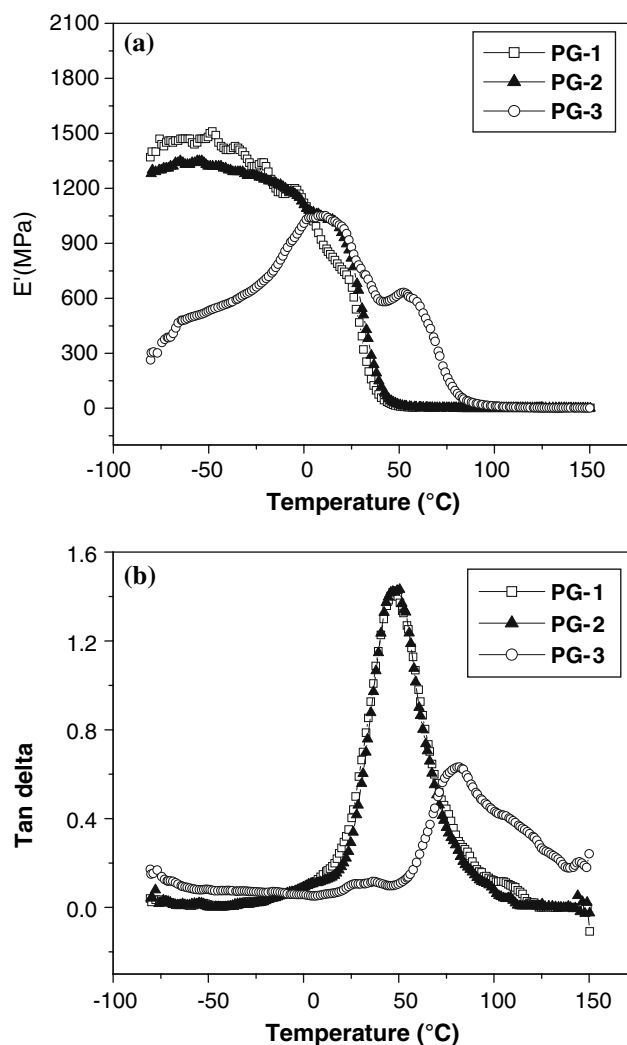


Fig. 3 DMA of samples (a) Storage modulus versus temperature (b) Tan delta versus temperature, Heating rate: $5^\circ\text{C}/\text{min}$

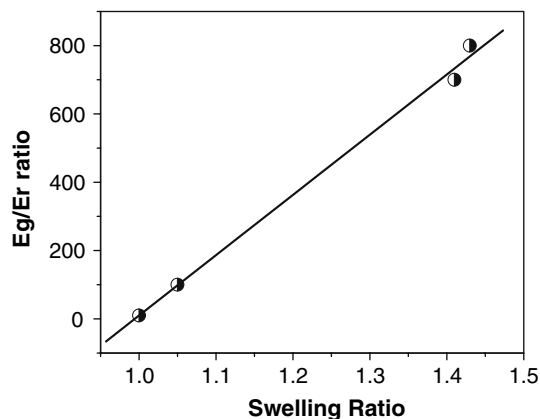


Fig. 4 Relationship between E_g/E_r ratios and swelling ratio

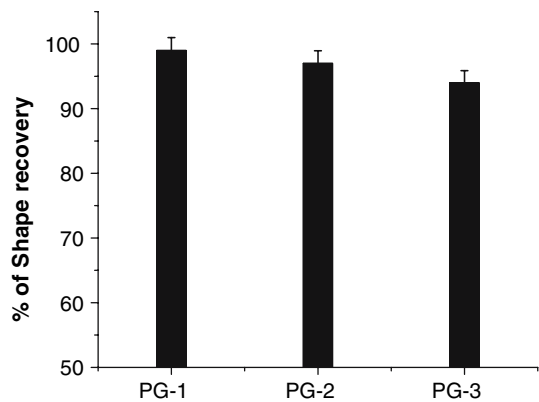


Fig. 5 Extent of Shape recovery of PTMO/poly(AA-co-AN) gels

Evaluation of shape memory property

The shape memory effect was quantitatively evaluated by bending test. Figure 5 shows the % of shape recovery of PTMO/poly(AA-co-AN) gel. All gels (PG-1, PG-2 & PG-3) exhibited more than 93% shape recovery. PG-4 lacked shape memory effect, consistent with its low modulus ratio and absence of PTMO complexation. The highest shape recovery of 99% was observed for PG-1 with highest E_g/E_r

ratio. The shape memory arises as a result of intermolecular H-bonding of the poly(AA-co-AN) gels with PTMO. The shape memory property is proportional to the H-bonding complexation promoted by high AA-content in the precursor copolymer. FTIR studies above and below T_g showed that the H-bond remains unaffected by temperature change. i.e. The strong H-bond interaction is retained at these temperatures.

Generally, shape memory polymer consists of two phases [17, 21], fixed phase and reversible phase. Fixed phases are due to entanglements or cross-linked points of the polymer chain and the reversible phase can be either crystalline or amorphous and contribute to the properties of elastomers-primarily recovery and energy absorption. In the present case, the reversible phase is constituted by PTMO complex, whereas the fixed phase is the chemical cross-links. The reversible phase transformation is essential for shape memory effect. In this case, the AA content in the precursor polymer decides the extent of complexation and the reversible phase transformation. Polymeric materials having shape memory properties can be designed by taking the polymer networks in which the polymer chains are able to fix a given deformation by cooling below a certain transition temperature (that can be a glass transition

Fig. 6 Shape recovery of Polymer gel complexes (a) PG-1 at 65 °C and (b) PG-2 at 70 °C at different time intervals



temperature or a melting temperature) [22]. In the present case, it is the glass transition temperature of complex that trigger the shape recovery property.

Shape recovery of the polymer gel complexes (PG-1 and PG-2) were demonstrated by taking a rod of dimension 50 mm length and 5 mm diameter. It was heated above T_g (PG-1 at 65 °C, PG-2 at 70 °C) and distorted and frozen in an ice bath. The deformed sample retained the shape at ambient temperature. Figure 5 shows extent of shape recovery. It increases with PTMO content in the complex. When heated to a temperature above T_g (PG-1 at 65 °C, PG-2 at 70 °C) using a hot plate, the shape was recovered in about a minute. The different stages of shape recovery of PG-1 and PG-2 are demonstrated in Fig. 6a and b. About 99% shape recovery with a modulus ratio of 168.2 and $\tan\delta$ magnitude 1.086 were observed for the reported H-bonded complex of poly (acrylic acid-*co*-methylmethacrylate) networks with polyethylene glycol [14]. Present system exhibited 99% shape recovery with an elastic modulus ratio and $\tan\delta$ maxima of 800 and 1.4 magnitude. The high modulus ratio implies fast recovery though it was not quantified. $\tan\delta$ maxima >1 implies high energy absorbing capacity which find potential applications of the developed system in vibration control area.

Conclusions

Polymer gels of [poly(acrylic acid-*co*-acrylonitrile)] were synthesized by varying compositions of AA and AN in the prepolymer, and complexing with PTMO to get PTMO/poly(AA-*co*-AN) complexed gels. The complexation occurred mainly through H-bonding of carboxyl group of acrylic acid with ether group of PTMO. The swelling ratio of PTMO/[poly(AA-*co*-AN)] gels increased and T_g diminished with enhancement in the acrylic acid-content. The modulus ratio (E_g/E_r) of the PTMO/[poly(AA-*co*-AN)] gels showed an increasing trend with the acrylic acid content,

which is conducive to better shape memory and shape recovery properties. All PTMO/poly(AA-*co*-AN) gels, exhibited more than 93% shape recovery. The highest shape recovery of 99% was observed for PG-1 with highest E_g/E_r ratio, resulting from enhanced H-bonding interactions.

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