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Characteristics of the creep-induced bending deformation of a PVC gel actuator by an electric field

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Abstract The influence of plasticizer (Dibutyl adipate) content on characteristics of creep-induced bending deformation of polyvinyl chloride (PVC) gel actuator was investigated in an electric field. The PVC gel bent to the anode side during the first electric field application. However, the gel quickly bent, and the bending deformation gradually increased to a stable state during the succeeding application of electric field. The measurement of space charge showed that a negative space charge gradually accumulated near the anode during the succeeding application of electric field. The dielectric constant of the gel also showed the above similarities. Such similarities suggest that PVC gel can memorize electrically induced deformation. On the other hand, the bending deformation, and the memory effect of the gel depended on the contents of plasticizer. Strong memory effect was obtained for lower content of plasticizer which indicated an influence of the density of the PVC chains and the alignment of PVC dipoles for orientation conformation in the gel network on the characteristics of creep-induced bending actuation and the memory effect of the PVC gel actuator in an electric field.

Introduction

In recent years, polymer actuation materials have been much paid attention and applied to various field because of their structural features and ability to response under various types of external stimuli such as pH, temperature, light, and magnetic or electric field [1–10]. Actuation materials using dielectric polymers particularly have good efficiency at energy conversion and durability for longer time as compared to typical actuation materials, including polyelectrolytes, ionic, and conductive polymers. We have been investigating electrical actuation of soft dielectric polymers such as plasticized poly(vinylchloride) (PVC gel) for the development of polymer actuators as artificial muscle. PVC gel a jelly like soft material containing a large amount of plasticizer, shows a very unique deformation in an electric field. PVC gel creeps on the anode surface when an electric field is applied and quickly recovers when the electric field is removed. This electrical deformation is called pseudopodial amoeba-like creep deformation, since it has analogy to the pseudopodial motion of amoeba [11]. Using this creep deformation various actuation motions such as bending, sliding, and oscillation have been enabled by our laboratory group controlling arrangement of electrode and gel [12]. We have already developed focus-controllable lens and micro finger devices [13]. In our previous papers, we have reported on actuation mechanism, local layer structure formed near the anode, and internal structure of the PVC gel during actuation in an electric field [14–16]. The results focused on the force generated between electrodes and plasticizer migration from cathode to anode. However, the characteristic of creep-induced motion of PVC gel during actuation has not been investigated.

Shape memory materials are the stimuli-responsive materials that can memorize their shapes and revert to their permanent shape upon application of an external stimulus. Polymer gels react to changes in the external conditions by considerable volume changes, swelling, or shrinkage, and show memory effect. Hydrogel with hydrophobic

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crystallizable side chains and cross-linked poly(vinyl alcohols) show a thermoresponsive one way-shape memory effect [17, 18]. Dielectric film like polyurethane elastomer shows memory effect during bending deformation, that is, once the film bend to a direction, then it bends to the same direction against the polarity right after the inversion of polarity of the applied electric field [19]. As PVC gel is a dielectric polymer gel, and it shows unique deformation in an electric field, the similar memory effect has been expected during the electrical actuation of PVC gel.

In this article, we reported the influence of plasticizer (Dibutyl adipate) content on electromechanical behaviors of PVC gels during succeeding application of an electric field. The purpose of this study was to understand the mechanism and the characteristics of the creep-induced bending deformation of PVC gels in an electric field. The creep-induced bending deformation increased with increasing plasticizer addition to the PVC and the leak current also increased. When an electric field was applied, PVC gel bent to the anode using its creeping motion and the gel quickly recovered when the electric field was removed. However, the bending deformation gradually increased by repetitive application of electric field and finally reached to a stable state. The space charge density and dielectric constant were measured and it was found that the space charge is closely related to the characteristic during bending deformation of PVC gel. Such similarities suggest a memory effect of PVC gel during electrical actuation. The memory effect depended on the content of plasticizer and PVC gel made with lower content of plasticizer showed strong memory effect. All of the results indicated an influence of PVC chains in the gel network on the characteristics of creep-induced bending actuation and the memory effect of PVC gel actuator in an electric field.

Experimental

Materials

PVC gels were prepared from commercial PVC powder ($M_n = 99000$ g mol^{-1}, $M_w = 233000$ g mol^{-1}, $n = 3728$), tetrahydrofuran (THF) and dibutyl adipate (DBA). DBA is a typical plasticizer. PVC powder was dissolved in a THF/DBA mixture, then the solution was cast in a PTFE laboratory Petri dish. THF was evaporated at room temperature for 3–5 days to prepare a soft, transparent PVC gel. The weight ratios of PVC to DBA were adjusted to 1:3, 1:5, 1:7, and 1:9: the gels are denoted DBA3, DBA5, DBA7, and DBA9, respectively. The thickness of the PVC gel was used to be in the range 300 μm to 1.5 mm.

Measurement of bending actuation and current

The PVC gels obtained were sandwiched between anode and a cathode. The gels were cut into 5 × 15 mm^2 rectangular pieces; these were used for measuring the bending actuation in an electric field. The measurements were carried out using the experimental setup shown in Fig. 1. The gel was vertically suspended in air, and the top of the gel was fixed between anode and cathode. During application of the electric field, the displacement of the gel's free end was measured with a Keyence LB-62 laser displacement meter. The application of the electric field and the measurement of the current were carried out with an Advantest R8340A ultrahigh-resistance meter. All the measurements were conducted at room temperature. Applying a DC voltage up to 1000 V mm^{-1} triggered the bending motion of PVC gels.

To measure current of DBA only and DBA with PVC powder, A reagent electric response test was carried out as per set up shown in Fig. 2. PVC powders were put into DBA liquid, and set between two electrodes in an electric field. The distance between the two electrodes was 10 mm and the applied electric voltage was 1000 V.

Compressive strength measurement

Thermal mechanical analyzer (TMA) was used for the measurement of compressive modulus of the PVC gels. A compressive probe of 9.348 mm^2 area was used to apply a constant compressive load of 500 mN/min. The gels were cut in a circular shape of 10 mm diameter and 700 μm–1.4 mm in thickness and placed on the platform. The measurements were carried out at room temperature.

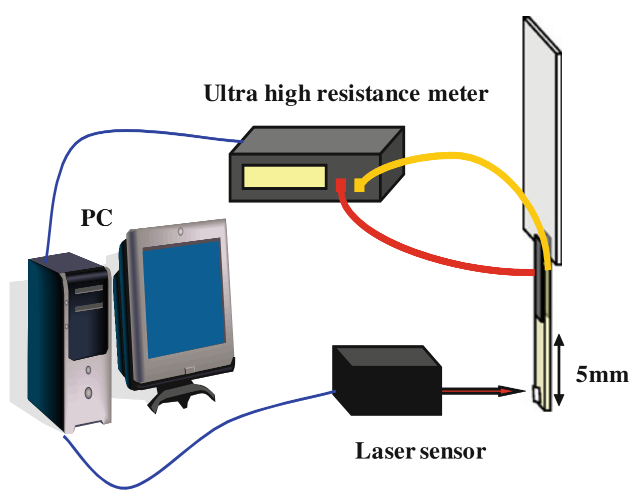

Fig. 1 Experimental set up for the measurement of bending displacement of PVC gel using laser displacement sensor and current was measured by ultra high resistance meter

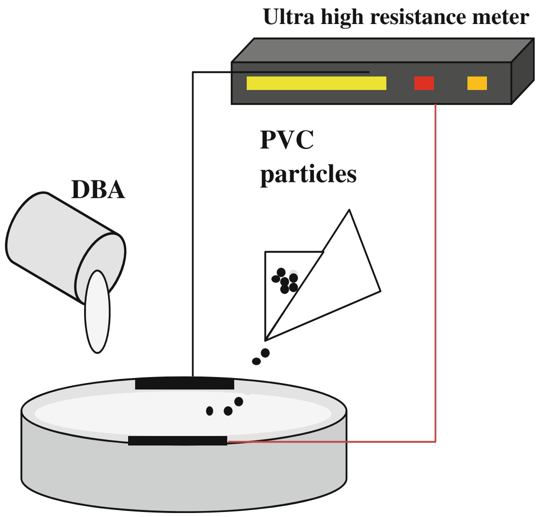

Fig. 2 Set up for reagent electric response test

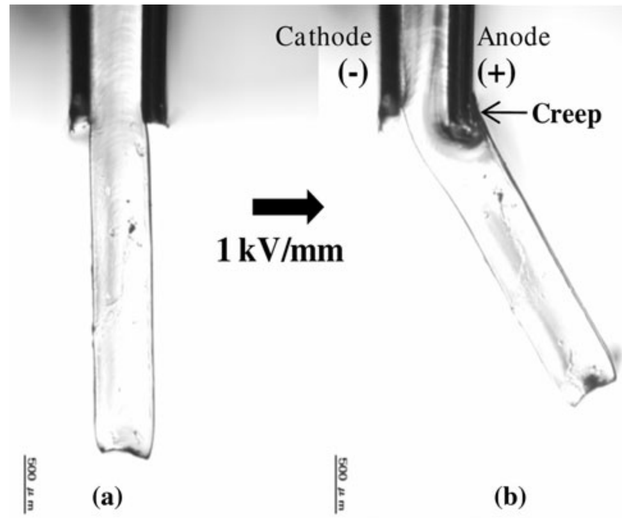

Fig. 3 The actuation of PVC gel (**a**) before application of an electric field; and (**b**) creep-induced bending motion in 1 kV mm^{-1} electric field

Measurement of the space charge distribution

The space charge distribution in the PVC gels was measured with a Five Lab Co., Ltd. pulsed electroacoustic nondestructive test system. Samples with diameter 10 and 1 mm in thick (larger than the sensor diameter) were carefully placed between the electrodes with normal pressure. The distribution of the space charge density was obtained when an electric field was applied at room temperature. The applied electric field and pulsed voltages were 1000 V mm^{-1} and 600 V, respectively. The electric field was applied for 60 s and repeated after 30 s interval.

Dielectric spectroscopy

The apparatus used was a model SI-1260 dielectric/Gain-Phase Analyzer coupled with a model 1,296 dielectric interface (Solartrin Analytical Co., Farnborough, UK). Data was collected by a PC and analyzed with software (Zplot and Zview). Dielectric measurement was performed at sweep frequencies from 10^0 to 10^6 Hz (five points/decade) with signal amplitude 100 mV for DBA9 sample repeatedly, at room temperature. The PVC gel was placed between two parallel plate electrodes and thickness was measured by a digital thickness meter. Circular disk-shaped specimens about 13 mm in diameter (larger than the electrode diameter) and 600 µm to 1 mm thick were used.

Results and discussion

Creep-induced bending deformation of PVC gels

When an electric field was applied to the PVC gel, it bent to the anode side using creep deformation (Fig. 3). The creep-induced bending displacement of PVC gels was measured by laser displacement sensor. Figure 4 shows bending displacement of PVC gels containing various DBA content. The duration of applied electric field was 60 s at the field ranged 500–1000 V mm^{-1}.

It was observed that the bending displacement increased with increasing plasticizer content and the sample DBA9 showed the highest bending displacement. By removing the field, all gels were restored completely to its original position instantly. The bending and restoring cycle was reproducible, showing that the PVC gel is a good elastic body under the experimental conditions. Figure 4b shows the bending displacement of different PVC gels as a function of electric field. The bending displacement increased with increased electric field almost linearly and DBA9 gel also showed the highest bending displacement at all electric fields. The results were directly related to the mechanical properties of the PVC gels. Figure 5 shows the stress–strain curves for DBA3, DBA5, DBA7, and DBA9 gels under compressive mode.

The elastic modulus decreased and PVC gels become softer and softer with increasing DBA content. The sample DBA9 showed the highest strain at all applied stress than that of other gels and also showed the highest bending displacement during the electrical actuation. According to the bending displacement diagram, although PVC gels are very soft, but represent a good liner response when the electric field was applied. The mechanism of the bending deformation has been reported by the charge migration from cathode to anode and charge accumulation near the anode. Creep occurs as a result of repulsive forces of the accumulated space charges [20]. Figure 6a shows charge migration of DBA9 gel from cathode and charge accumulation near the

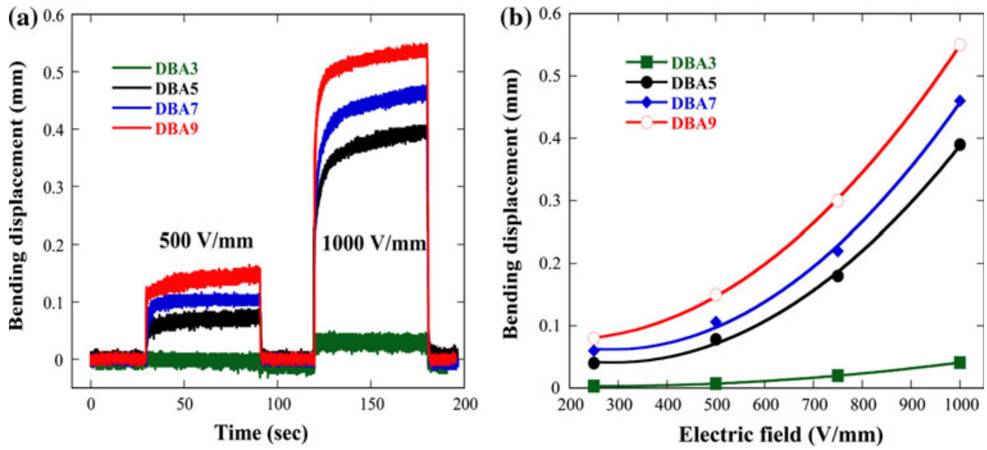

Fig. 4 The bending displacement of PVC gels with four different DBA content (**a**) in applied electric field of 500 and 1000 V/mm and (**b**) at different electric fields

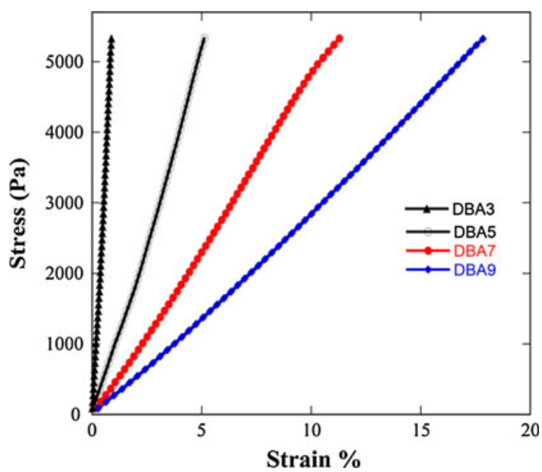

Fig. 5 Mechanical properties of PVC gels with varying DBA content

anode. The accumulated charge density depended on the content of DBA to PVC. The area of the accumulated space charge density of four PVC gels was measured as a triangle, and the values were plotted in Fig. 6b.

The result shows that the accumulated negative charge density was the highest in DBA3 gel and according to the mechanism of creep deformation, the repulsive force of the accumulated charges is the highest but due to the highest modulus of the gel it exhibited the least bending displacement among four samples. The observation concludes that softer the gel easier the creep-induced bending deformation in an electric field even with less space charge density. However, the bending actuator usually produces a lower blocking force [21]. To judge the actuator performance of DBA9 gel, the blocking force was measured to assess mechanical power output at different applied electric fields. The mechanical power output as a function of electric field with thickness variation of DBA9 gel is shown in Fig. 7.

The output power increased with increasing the magnitude of electric field and depended on the thickness of the gel. The thick gel showed better actuator performance in terms of mechanical power output than thin gel which is attributed to the modulus of rigidity of the gel. Similarly, since DBA9 gel is soft, the comparison on the mechanical power output for PVC gels containing various weight rations of PVC to DBA is not beneficial. The efficiency of the PVC gel actuator can be measured from the ratio of mechanical power output and the electrical energy consumption.

Energy consumption of PVC gels

The PVC gels bent in an electric field consuming with micro to nano ampere electric current as the gels was not prepared with any ionic species. Considering micro to nano ampere current consumption during electrical actuation, PVC gels are highly efficient at energy conversion. The leak current of PVC gels depended on the plasticizer content. Figure 8 shows leak current of four PVC samples. DBA9 gel showed the largest initial leak current than other gels. The leak current increased with increasing electric field intensity. Another way to look at the characteristic of current consumption during actuation is that the initial leak current was jumped suddenly and gradually decreased with the passing of time to a steady state. The behavior of current consumption indicates that initial charges are carried by ionic like impurities and after sometime charges are separated. The mechanism of charge transfer during the actuation of PVC gels is still unknown. In order to understand the process of charge transfer in PVC gels, regent electric response test were carried out.

For pure PVC, there was no current consumption but for pure DBA, nanoampere level current consumption was observed. Though the direct charge transfer does not occur in dielectric solvent like DBA, but when electric field was applied to DBA, electric field-induced flow of DBA occurred to anode and current flows. This observation indicates that PVC does not carry charges and some

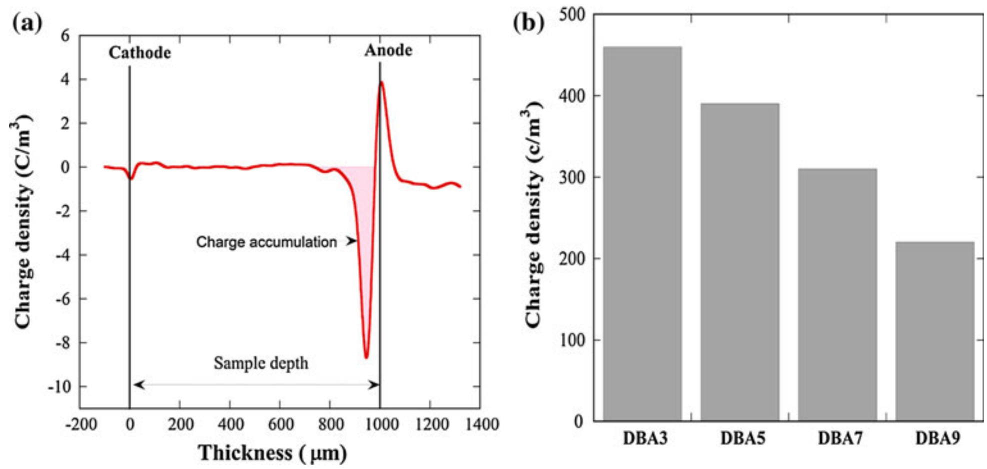

Fig. 6 The space charge distribution of DBA9 gel (**a**), and (**b**) calculated area of charge accumulation of four PVC samples

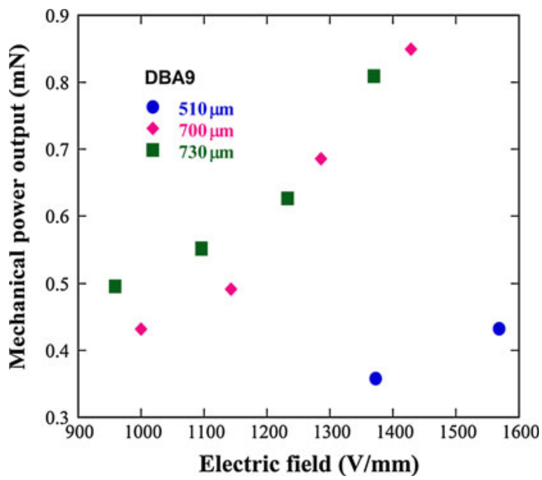

Fig. 7 Mechanical power output of DBA9 gel as a function of electric fields with thickness variation

charges are injected in DBA but what kind of chemical structure induced by the electric field has not been investigated yet and it is very difficult to measure qualitative information about electrochemical reaction occurs in DBA by cyclic voltammeter due to very short life time. The charges carried by the DBA molecules during the actuation of PVC gels and as a result, higher current consumption was observed in PVC gels with higher DBA content. In reagent electric response test, when PVC powder was added to the DBA, the current consumption was increased. The result can be explained as dehydrochlorination of PVC in DBA. It is known that under heat and light, hydrogen chloride is produced by dehydrochlorination and similar process is expected during the actuation of PVC gel in an electric field.

Characteristics of creep-induced bending of PVC gel

According to the electromechanical behavior of PVC gels discussed above, the influence of plasticizer content on creep-induced bending motion and current was evident. It is necessary to study characteristics of creep-induced bending motion of PVC by repetitive application of electric field in order to utilize the PVC gel as a practical actuator. Figure 9 shows the characteristics of DBA9 gel in repetitive application of 1 kv/mm electric field obtained from the laser displacement sensor during bending displacement. When the electric field was applied to DBA9 gel, it bent

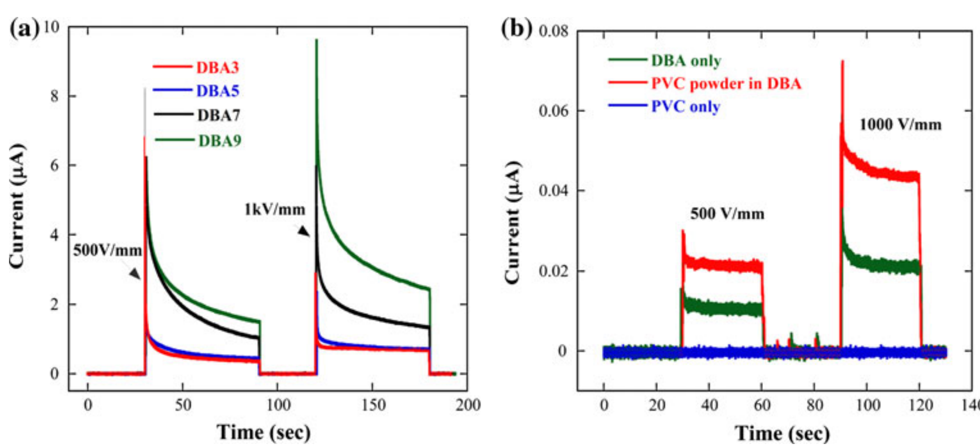

Fig. 8 The leak current consumption of PVC gels with four different DBA content (**a**); and reagent electric response test (**b**) in applied electric field of 500 and 1000 V/mm

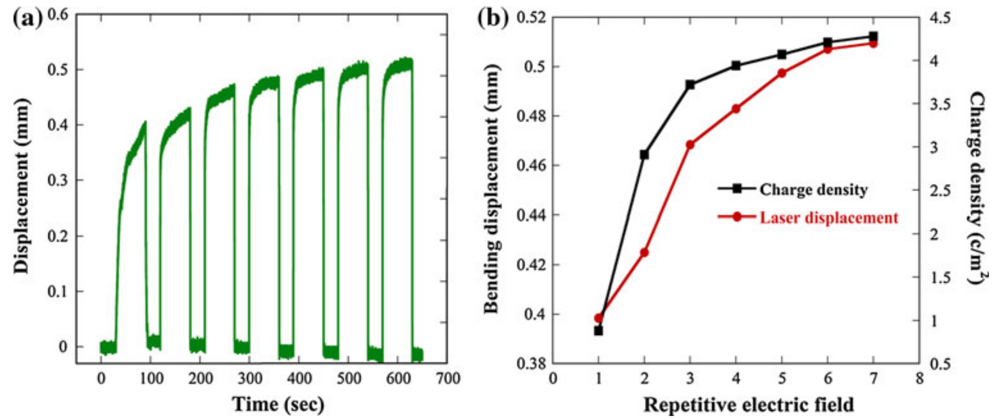

Fig. 9 The memory effect during bending displacement of DBA9 gel in an applied electric field of 1000 V/mm (**a**) and relationship between space charge density and bending displacement of DBA9 gel by repetitive application of electric field of 1000 V/mm (**b**)

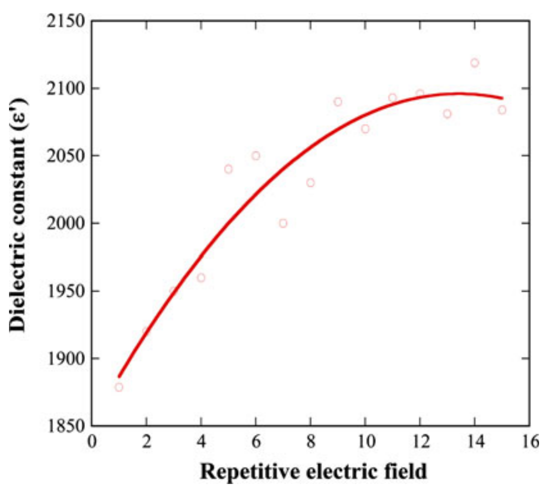

Fig. 10 Dielectric constant of DBA9 gel at frequency 1 Hz by repetitive application of electric field

about 0.4 mm to the anode and the gel quickly recovered when the electric field was removed. Further application of electric field after 30 s for a same period increased bending displacement than the previous one. By repetitive application of electric field, bending displacement gradually increased and finally reached a stable state. This phenomenon is considered as a kind of memory in which an electric field reminds the PVC gel of the electrically memorized strain.

As shown in Fig. 9a, the response speed during the second and subsequent application of electric fields was much faster than that during the first application. The memory effect provides two advantages; applying same electric field higher electrical actuation can be obtained or intensity of applied electric field can be reduced for a desired actuation. The measurement of space charge also shows that negative charge density gradually accumulated near the anode during the succeeding application of electric field (Fig. 9b). The memory effect was also observed in dielectric properties of PVC gel. Figure 10 shows dielectric constant of DBA9 gel at frequency 1 Hz by repetitive application of electric field.

The dielectric constant gradually increased up to several cycles and after that became stabilized. The dielectric phenomena of PVC gel can be explained from the polarization of the PVC chain in an electric field. From the viewpoint of molecular structure, both PVC and DBA of PVC gel are dipolar due to the existence of C–Cl and C=O bonds and in the presence of an electric field the dipoles attempt to become aligned with the field [22]. The dipole alignment creates polarization of the PVC chains and repetitive application of electric field increased alignment of dipoles to optimal polarization gradually. The alignment of PVC dipoles toward the anode makes an orientation conformation, which does not disappear immediately after switching off the electric field. The conformation enhances electrical actuation of PVC gels during the succeeding application of electric field. The same polarization phenomenon was also observed in the space charge measurement.

Another unique characteristic is the bending direction and the polarity of the applied electric field. Figure 11 shows bending displacement of DBA9 and DBA3 gel in an applied electric field of 1 and 3 kV/mm, respectively, with polarity change.

DBA9 gel did not bend any direction for a while during the application of inverted electric field and bent to the opposite direction at the end of the duration but DBA3 memorized the direction of bending strongly and bent to the same direction right after the inversion of polarity of the applied field and gradually changed bending direction. The consumption of electric current increased to a maximum right after the inversion of polarity of the applied electric field for both DBA3 and DBA9 gel. The result may be due to the re-orientation of dipoles on the PVC chains in gel network after the inversion of polarity. The re-orientation of dipoles is easier and faster for PVC gels with higher DBA content due to the flexibility of PVC chains.

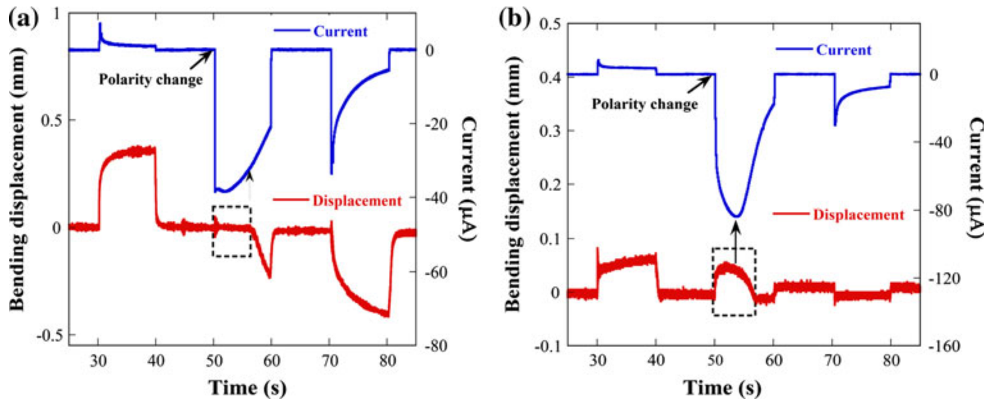

Fig. 11 Bending deformation of DBA9 gel (**a**) and DAB3 gel (**b**) in applied electric field of 1 and 3 kV/mm, respectively, with polarity change

The memory remains for longer time in case of DBA3 gel than DBA9 gel and disappears by repetitive application of the inverted electric field. The reason for the bending direction was not changed by reversing the polarity of an applied electric field can be explained as follows, although the details of the mechanism are still under investigation, that is the bending electrostriction causes the bending deformation. According to the definition of bending electrostriction, the deformation D follows by the relation:

$$D = ME^2$$

where E is the applied electric field and M is a bending electrostrictive constant. Because $(-E)^2$ is equal to E^2, the bending direction does not change with a reverse of the electric field polarity [23]. All phenomenon during the creep-induced bending actuation of PVC gel is due to the fact that as the DBA content decreases, the density of PVC chains per unit area or volume in the PVC gel increases so as to increases the number of free dipoles on the PVC chains, resulting in the great effects on the creep-induced bending characteristics of PVC gel actuator.

Conclusion

In summary, the influence of plasticizer (Dibutyl adipate) content on the characteristics of creep-induced bending deformation of PVC gel actuator was investigated in an electric field. The bending deformation and leak current increased with increased plasticizer addition to the PVC. Space charge distribution, dielectric constant, and elastic modulus were measured in order to understand the mechanism and characteristics of the bending deformation. The bending deformation depended on the elastic modulus of PVC gel but not on the space charge density. Moreover, the bending deformation became faster and faster to a stable state during succeeding application of electric field. The space charge density and dielectric constant supported the characteristics of bending deformation of PVC gel during the succeeding application of electric field. Such similarities suggest a memory effect of PVC gel. The memory effect depended on the content of plasticizer in PVC gel and found strong memory effect for lower DBA content, which was considered to originate from a confirmation of PVC dipoles orientation toward the anode, which exists even off state of first electric field application. The influence of PVC chains density is also evident on the characteristics of creep-induced bending deformation of PVC gel actuator in an electric field.

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References

1. Heijl JMD, Du Prez FE (2004) Polymer 45:6771
2. Kim SJ, Spinks GM, Prosser S, Whitten PG, Wallace GG, Kim SI (2006) Nat Mater 5:48
3. Tsutsui H, Akashi R (2006) J Polym Sci Part A Polym Chem 44:4644
4. Dong L, Agarwal AK, Beebe DJ, Jiang H (2006) Nature 442:551
5. Moniruzzaman M, Fernando GF, Talbot JDR (2004) J Polym Sci Part A Polym Chem 42:2886
6. Tatsuma T, Takada K, Miyazaki T (2007) Adv Mater 19:1249
7. Nersesse N, OR SW, Carman GP, Mccall SK, Choe W, Radousky Harry B, Mcelfresh Mike W, Pecharsky VK, Pecharsky AO (2004) Appl Phys Lett 84:4801–4803
8. Osada Y, Okuzaki H, Hori H (1992) Nature 355:242
9. Takada K, Tanaka N, Tatsuma T (2005) J Electroanal Chem 585:120
10. Boczkowska A, Awietjan SF (2009) J Mater Sci 44:4104. doi:10.1007/s10853-009-3592-7
11. Md. Zulhash U, Masaki Y, Watanabe M, Shirai H, Hirai T (2001) Chem Lett 30: 360
12. Md. Zulhash U, Watanabe M, Shirai H, Hirai T (2003) J Poly Sci Part B Poly Phys 41: 2119
13. Hirai T, Ogiwara T, Fujii K, Ueki T, Kinoshita K, Takasaki M (2009) Adv Mater 21: 2886
14. Xia H, Takasaki M, Hirai T (2010) Sens Actuators A157:307
15. Xia H, Hirai T (2010) J Phys Chem B114:10756
16. Xia H, Ueki T, Hirai T (2011) Langmuir 27:1207

17. Hirai T, Maruyama H, Suzuki T, Hayashi S (1992) J Appl Poly Sci 45:1849
18. Hirai T, Maruyama H, Suzuki T, Hayashi S (1992) J Appl Poly Sci 46:1449
19. Watanabe M, Hirai T (2004) Jpn J Appl Phys 43:1446
20. Zulhash Uddin M, Watanabe M, Hirofusa S, Hirai T (2002) J Robotics Mechatronics 14:118–123
21. Tao Li, Chen YH, Ma J (2009) J Mater Sci 44:5393. doi: 10.1007/s10853-009-3567-8
22. Ramesh S, Leen KH, Kumutha K, Arof AK (2007) Spectrochim Acta Part A66:1237
23. Masashi W, Makoto S, Yoshiyuki H, Hirofusa S, Hirai T (2001) J Appl Poly Sci 79:1121