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**Paper:**

# Creeping and Novel Huge Bending of Plasticized PVC

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**We actuated poly(vinyl chloride) (PVC) gel by applying a dc field, and found localized creeping deformation, which induced swift, huge bending like a joint. The bending angle reached ca.150° at maximum at the field of 1000 V $mm^{-1}$ with the velocity of ca. 90° $s^{-1}$. The electric current was very small and in the range of 68 nA $cm^{-2}$. The mechanism of reversible, marked bending was studied using blocking and contact electrodes. The gel consisted of PVC and dioctyl phthalate (DOP), and was free of electrolytes. The concept is simple and applicable to conventional polymer materials. It could serve for developing new classes of soft and durable mechanically functional materials.**

**Keywords:** poly(vinyl chloride) gel, creep induced bending, artificial muscle, electrotactic, electric field

## 1. Introduction

Great efforts have been devoted to development and fabrication of potential actuators from polymer gels as intelligent materials for artificial muscles, sensors, and controlled drug-delivery.[1-9] Stimuli sensitive polymer gels can respond to changes in environmental conditions such as temperature[10], light[9], pH[11], electric field[1,2,5,6] and they vary volumes and shapes. Hence, polymer gels have received special attention as soft mechanically functional materials. Katchalsky et al.[12] demonstrated chemomechanical collagen gel fibers thermodynamically capable of transforming chemical energy to mechanical work. Tanaka et al.[9] reported the phase transition in polymer gels induced by visible light. Osada et al.[5] actuated a polyelectrolyte gel by applying a dc. electric field. In electrical actuation of polymer gels, most investigations were conducted on polyelectrolyte gels since they contain ionic species that induce deformation under an electric field. In the polyelectrolyte gels, different actuations have been proposed, and in most cases water or salt solution is necessary for phase transition or deformation. Applications are limited in low voltage and current, as the gas, or heat generation by electrolysis is usually unavoidable. We studied electrically stable polymer gels as soft mechanically functional materials that can be applied in air or in the absence of water, completely different gel actuation. Little attention was paid to electrical actuation of nonionic polymer gels except poly(vinyl alcohol)-dimethyl sulfoxide gel (PVA-DMSO gel)[13], since they are inactive in an electric field due to the absence of ionic species.

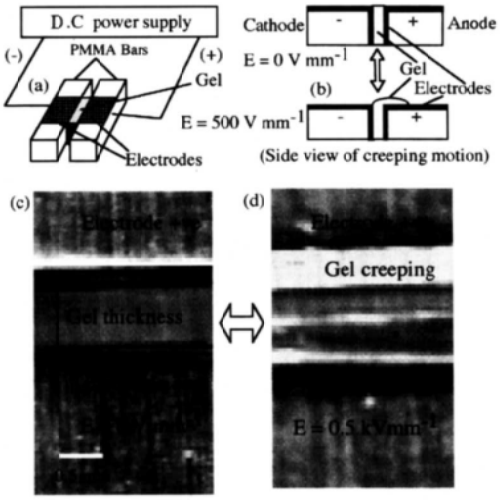


**Fig. 1.** (a) Experimental setup used for creeping motuon. The gel is placed between a pair of electrodes, which is supported by two poly(methylmethacrylate) (PMMA) bars. The top of the gel is adjusted flat to the level of electrodes. (b)An illustration of the side view of creeping motion. (c)No creeping of gel with E = 0 Vmm$^{-1}$. (d)The gel is creeping onto the anode with E = 500 V mm$^{-1}$.

We detail motions of creeping and large bending of PVC-DOP gel and the mechanism of motion.

## 2. Experimental Section

### 2.1. PVC-DOP Gel Preparation

Commercial grade PVC, whose degree of polymerization is 1000 (molecular weight = 62500) and was supplied by Sun Arrow Chemical Co. Ltd., was purified by a conventional reprecipitation method, using tetrahydrofuran (THF) and methanol. After 3 repetitive solubilizations and precipitations, purified PVC was obtained. The purified PVC is plasticized with DOP, a typical plasticizer. PVC was dissolved with DOP in THF solvent and cast and kept in a Petri dish at ambient temperature for 1 weeks to completely evaporate THF and yield a physically crosslinked PVC-DOP gel sheet 0.75 mm thick. PVC-DOP gel is transparent and homogeneous, contain-

ing 90 wt% plasticizer in the gel. No ionic components were added. The gel maintains its shape and behaves as an elastic nonionic gel. No leakage of DOP was observed and the gel was stable for more than 20 months in air at ambient temperature.

### 2.2. Experimental Setup

Applying a dc. voltage up to 1000 V $mm^{-1}$ triggered the motions of the gel. **Fig.1(a)** shows the experimental setup used for the creeping motion. We observed creeping and bending with a CCD camera under a microscope and the images were recorded by a video recorder at a rate of 30 frames s-1 and analyzed by using a personal computer (**Fig. 2**). The current was measured using an ampere meter (Advantest Crop. R8340A Ultra High Resistance Meter). The measurements were conducted in air at room temperature.

## 3. Motions of Creeping and Joint-Like Bending

### 3.1. Creeping Motion

A stripe of the gel, 10 mm long, 10 mm wide and 0.75 mm thick was cut, and first the gel was placed between a pair of electrodes (aluminum foil, 5μm thick). When an electric field (dc. and 500 V $mm^{-1}$) was applied, the gel is crept out onto the anode (**Fig.1(c)** and **1(d)**) and held deformation as long as the field was on (**Fig.1(b)**). Deformation was restored as soon as the field was turned off. Creeping is similar to pseudopodial-flow-induced deformation of biological cells such as an amoeba. **Fig.3** shows the time courses of current (μA) on the supply of electric field (V $mm^{-1}$) in creeping motion of PVC-DOP gel. The current (μA) increased proportionally with applied voltage (V $mm^{-1}$) in creeping. Creeping distance (mm) and creeping area ($cm^2$) increased with increasing the applied electric field (V $mm^{-1}$) (**Fig.4**). The relationship between creeping area andcurrent density (A $cm^{-2}$) was linear (**Fig.5**). The gel started creeping above 90 V $mm^{-1}$. The rate of creeping motion was fast. The creeping velocity (mm $s^{-1}$) increased proportionally with the applied electric field (**Fig.6**). For 1000 V $mm^{-1}$, the creeping velocity was 0.05 mm $s^{-1}$ and strain reached 1 mm. The electric field applied was far below the break down voltage (ca. 0.3 MV $mm^{-1}$). Strain reached more than 130% of the thickness of the gel.

### 3.2. Joint-Like Bending

For using creeping to bending, we changed the experimental set-up (**Fig.7(x)**). Here the gel was cut into a stripe with a size of 10 x 7 x 0.75 mm. Thin aluminum foil, 5μm in thickness, partly covered both sides of the gel surfaces as a pair of electrodes leaving 5 mm uncovered and exposed in air. The gel was fixed horizontally between two holder plates. In **Fig.7(x)**, five samples (Sample 1a/1b/1c/1d/1e) were prepared. In Sample 1a, each surface of the gel was covered with a thin aluminum foil (contact electrode). In Sample 1b, anode surface of the

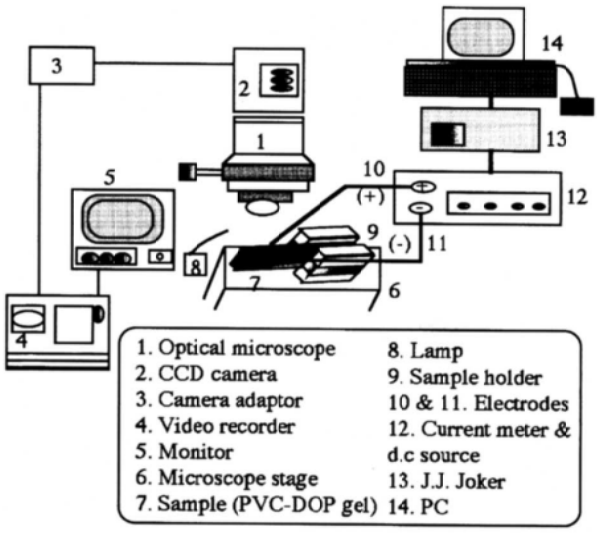


**Fig. 2.** Experimental setup used for the measurement of bending motion and current.

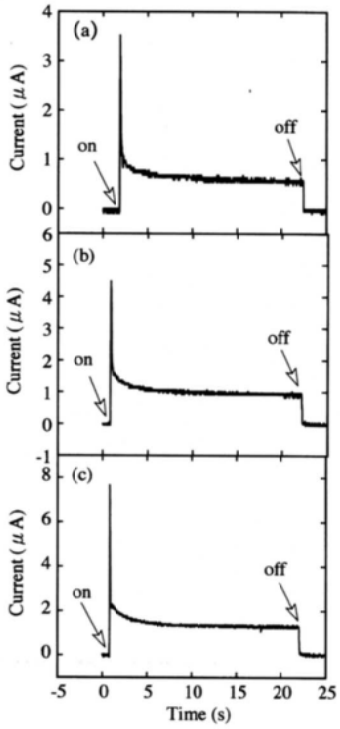


**Fig. 3.** Time courses of current (μA) on the supply of electric field (V $mm^{-1}$) in creeping motion of a PVC-DOP gel. (a) 300 $Vmm^{-1}$ (b)600$Vmm^{-1}$ and (c)900$Vmm^{-1}$.

gel covered with an aluminum foil and whole cathode was blocked with a polyethylene thin film insulating the gel from the aluminum electrode (blocking electrode). In Sample 1c, half of the cathode was blocked with a polyethylene thin film (partly blocked electrode). But in Sample 1d, half of the anode surface was blocked. In Sample 1e, the whole anode was blocked. In Sample 1a, when an

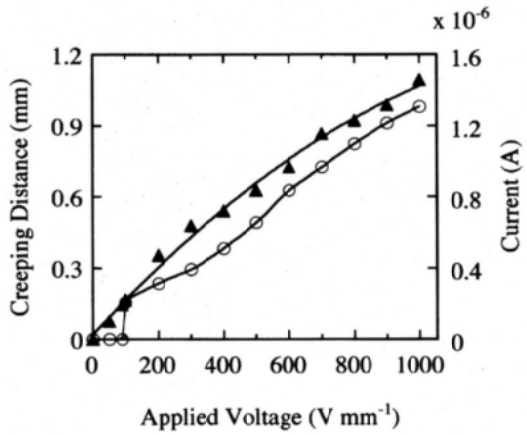


**Fig. 4.** Dependence of creeping distance (mm) and current (A) on the applied electric field (V $mm^{-1}$) in creeping motion of a PVC-DOP gel. ○ creeping dis -tance, ▲ current.

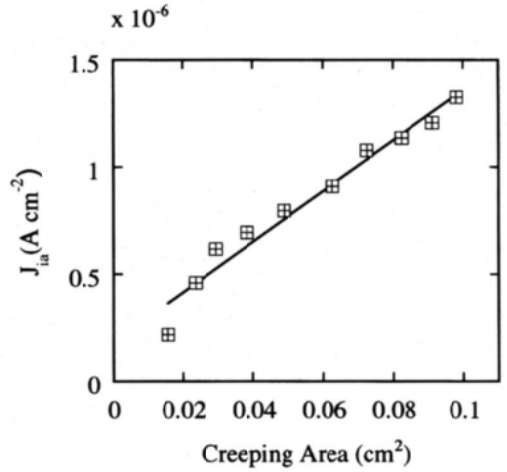


**Fig. 5.** Relationship between creeping area ($cm^2$) and current density ($J_{ia}$) in creeping motion of a PVC-DOC gel.

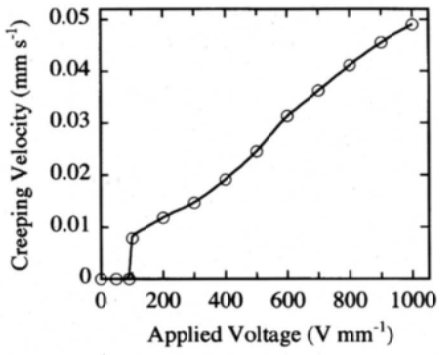


**Fig. 6.** Dependence of creeping velocity (Vmm $s^{-1}$) on the applied electric field(V $mm^{-1}$) of a PVC-DOP gel.

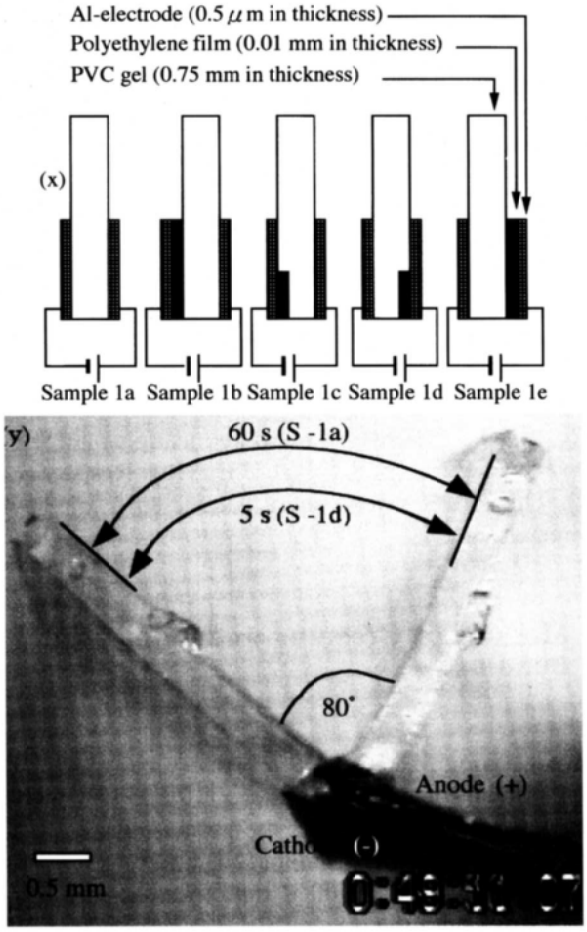


**Fig. 7.** (x) Fabrication of PVC-DOP gel/polyethylene lami-nate systems. (y) The bending motion of a PVC-DOP gel induced by the application of an electric field(500Vmm$^{-1}$). The overlapped image was composed of the beggining im-age and another one taken after 60s/5s in the Sample 1a/1d. The bending angle reached 80° after 60s/5s in the Sample 1a/1d, respectively.

electric field was applied to the gel, it bent joint-like to the anode side and reached the maximum steady state. The action was completed within 60 s at the field ranged from 300 to 1000 V $mm^{-1}$. The bending angle reachedca.100° at maximum at the field of 1000 V $mm^{-1}$. During the application of the field, the motion was sus-tained as constant after it reached steady state. The steady current was 66 nA $cm^{-2}$ at the field strength of 500 V $mm^{-1}$ (**Fig.7**). By removing the field, the gel was restored completely to its original position in 30 s. The bending and restoring cycle was reproducible, showing that the gel is a good elastic body under the experimental condi-tions. Sample 1b showed no bending with very small and irregular current (ca. 26 nA for 1000 V $mm^{-1}$). The result suggests that bending requires sufficient charge injection from cathode. In sample 1c, no strain was observed in the gel up to 800 V $mm^{-1}$ and much smaller bending (15° ) found after the application of 1000 V $mm^{-1}$ with small current (ca.46 nA). This result suggests insufficient charge injection from cathode. But in the case of Sample 1d, the bending was completed within 12 s at the field

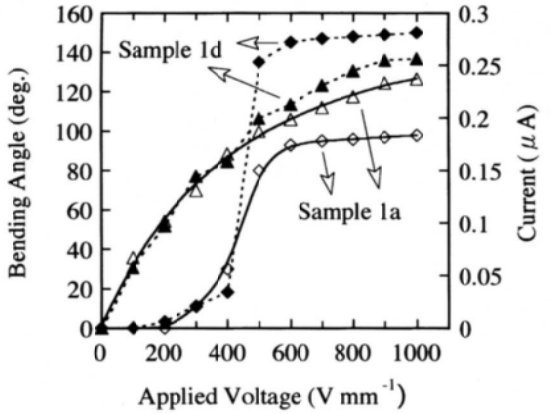


**Fig. 8.** Dependence of bending deformation (deg.) and current ( $\mu$A) on the applied electric field (V mm $^{-1}$) of PVC-DOP gel. ◇ / ◆ bending angle (deg.), △/▲ current for Sample 1a / 1d.

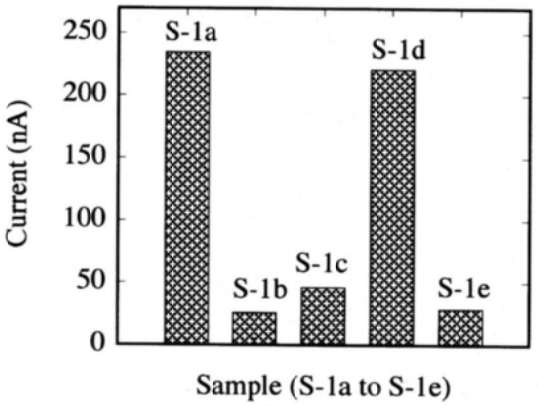


**Fig. 9.** Comparison of current (nA) observed among different samples in bending motion of PVC-DOC gel. The applied electric field was 1000 V mm$^{-1}$.

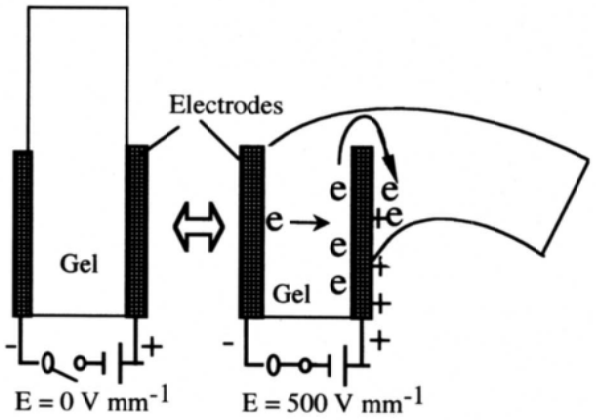


**Fig. 10.** The schematic illustration of bending mechanism of PVC-DOP gel.

ranged from 200 to 1000 V mm$^{-1}$. The bending angle reached ca.150° at maximum at the field of 1000 V mm$^{-1}$ with a maximum rate of 90° s$^{-1}$. In Sample 1e, no bending was observed with very small and irregular current (ca. 29 nA for 1000 V mm$^{-1}$). However, charge injection, which could be concluded to depend on the area of cathode and the electric field strength. The distribution of injected charges depends on insulation of anode side. These results strongly suggest that charge injection occurred on the cathode and caused bending (Sample 1d) on the anode by forming asymmetric distribution of injected charges. In Sample 1d, the level of asymmetric distribution of injectedcharges was the largest among samples studied, and hence very swift bending occurred. **Fig.8** shows the dependence of bending deformation (deg.) and current (μA) on the applied electric field (V mm$^{-1}$) in bending of the gel. The bending angle (deg.) increased proportionally to the square of the applied field only in the region from 300 to 500 V mm$^{-1}$ and saturated in the high field above 600 V mm$^{-1}$. But strain was not observed at the field strength below 200 V mm$^{-1}$ and 100 V mm$^{-1}$ in Sample 1a and 1d, respectively. The current increased with increasing applied voltage. **Fig.9** compares current (nA) observed among different samples studied in bending of the gel. The bending velocity (degree s$^{-1}$) of gel increased with increasing applied voltage (V mm$^{-1}$). The gel exhibited the velocity of ca. 7° / 90° s$^{-1}$ in sample 1a/1d.

## 4. Proposed Bending Mechanism

When either side of the electrode was insulated the bending was completely depressed, and when the cathode was partly insulated slight deformation was observed. When the anode was partly insulated, depression was not observed. From these results, we propose a tentative bending mechanism of PVC-DOP gel (**Fig.10**). Charges (electrons) injected from the cathode of the electrode into the gel migrate toward the anode and disappear by discharging. Before discharging on the anode, the accumulation of charges promotes electrostatic adhesiveness of gel onto the anode surface, and creeping deformation on the anode appeared (**Fig.1**). If the discharging rate on the anode is as swift as that on the cathode and no asymmetric charge distribution is exerted in the gel, neither bending nor asymmetric creeping motion can be expected. However, deformation induced in the gel is not a simple bending, but the bending induced by creeping deformation very much localized at the tip of the anode electrode (**Fig.10**). Negative charges in gel accumulated at the anode tend to spread contact with the anode, generate electrotactic strain by pulling the gel surface onto the other side of the aluminum electrode, and finally the gel is bent to the anode. When the field is off, the stickiness of the gel onto the anode disappeared by discharging, and the gel returns to its original shape by its intrinsic elasticity. The increase of an electric field leads larger deformation of the gel. Below the field of 200 V mm$^{-1}$ (Sample 1a) and 100 V mm$^{-1}$ (Sample 1d) charge accumulation were not enough for strain generation and lead the results (**Fig.8**).

## 5. Conclusions

Nonionic homogeneous PVC gel was found to creep or to be bent by applying an electric field with a very small electric current. The asymmetric distribution of injected charges is suggested for the interpretation of electrically induced motion. The concept of electrotactic deformation seems to be simple and applicable to conventional polymer materials. We anticipate that this strategy could serve as a method for developing new class of soft and durable mechanically functional materials to prepare micro machines, micro valves, actuators, and artificial organs in medical engineering.

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