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Graphene Oxide-Polyaniline Coating on Ionic Polymer Blend Membrane for Actuation

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Ionic polymer metal composites (IPMC) can be used as actuators and sensors and intrinsically have low activation voltage and large bending strain, which help to transform electrical energy to mechanical energy and can be utilized as bidirectional material. In this study, the ionic polymeric blend films/membranes of PVDF:PSSS:PVP in the blend ratio of 40:30:30; 50:30:20 and 60:15:25 (wt.%) is presented. The membranes were prepared by solution cast technique and coated with graphene oxide (GO)-polyaniline (PANI). Membranes were characterized by X-ray diffraction, optical microscopy. Electrical conductivities at different frequencies and water uptake properties were also determined. The actuating performance of PVDF:PSSS:PVP and water uptake of blend membrane was found to be maximum for the blend ratio of 60:15:25. PVDF:PSSS:PVP with blend ratio (60:15:25) also exhibited highest actuation at 10 V DC. Graphene oxide was prepared and characterized by using FTIR and Raman spectra. A brief account of the fabrication of IPMC and its actuation application was also presented.

Keywords: Actuator, Graphene oxide, Polyaniline, Conductivity.

INTRODUCTION

Actuators are primarily smart electro-mechanical devices which respond to external stimuli of electrical field in the form of mechanical movement [1,2]. The reverse phenomenon is also observed, *i.e*. if the device is subjected to mechanical movement then voltage is generated. Amongst many developed varieties of actuators, electroactive polymers (EAPs) have attracted much attention due to their several advantages [3-7]. Further advancement in the field of EAPs led to development of ionic polymer-metal composites (IPMCs), which comprise of a polymer film sandwiched between two metallic electrodes. Several researchers [8-10] have successfully reported electro-mechanical actuators based on carbon nanotubes (CNTs), conductive polymers and graphene. Introduction of CNTs into the electrode layers improves electromechanical performances; like respond speed and strain (stress) generating rate of i-EAP (ionic electroactive polymers) [9]. Hata *et al.* [11] have reported second-generation dry i-EAPs actuators using super growth SG-SWNTs as electrodes. However, due to the lack of perfect electrode material and efficient synthesis method, the fabrication of i-EAP actuators having superfast response and ultra-high mechanical output abilities still a great challenge. Conductive polymers such as polypyrrole, polythiophene and polyaniline can be electrochemically oxidized and reduced *i.e*. having reversible redox reaction [12]. This resulted in a volume change of the material caused by the ingress and egress of ions and solvent from the electrolyte. It is further reported that fullerene, graphene or its oxides could be used as filler of composite film for actuators [13].

An *et al*. [14] reported the macroscopic assembly of graphene oxide and MWCNT bilayer improves the humidity and/or temperature dependent actuation behaviours. Actuators based on polymer ion-exchange membranes exhibit large bending displacement (1-10 mm) at low applied voltage (1-5 V) and have different properties such as flexibility, light weight

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and biocompatibility [4,15-18]. Many research efforts have been made to add rGO, CNT and other nanoscale materials into the polymer matrix and developed composite materials used as the actuator materials [19].

Ionic polymer composites (IPC) actuators have different advantages over the traditional electroactive polymers or ionic polymer metal composites actuators because of good input response, light weight, small structure, high efficiency of power transition, *etc*. [8-10]. These materials can also be used as micro-robots used underwater, swimming micro-robots and walking micro-robots [11-13]. The aim of this research article is to develop and characterize polymer blend membrane for the actuation purpose which actuate in air at low voltage (DC). In this article, polymer blend membranes using PVDF:PSSS:PVP with the blend ratio of 40:30:30, 50:30:20 and 60:15:25, coated with graphene oxide-polyaniline, have been studied for their application of actuators. The membranes have been characterized by X-ray diffraction and optical microscopy. The electrical conductivities at different frequencies were also measured.

EXPERIMENTAL

Aniline was acquired from Fisher scientific, graphite powder, toluene (sulphur free), *N*,*N*-dimethylformamide (DMF) while cupric sulphate pehtahydrate ($CuSO_4 \cdot 5H_2O$) were acquired from Qualikems. Polyvinylidene fluoride (PVDF), poly (sodium 4-styrene sulfonate) (PSSS), poly(vinyl pyrrolidone) (PVP) and lithium chloride from Sigma-Aldrich. All the chemicals were of AR grade and used without any further purification. Double distilled water was used as per the requirement.

Synthesis of graphene oxide (GO): Synthesis of graphene oxide using modified Hummers method [20] is shown in Fig. 1. Graphite flakes were used to prepare graphene oxide (GO) using modified Hummer's method. In brief, a mixture of graphite flakes (2 g) and $NaNO_3$ (2 g) and H_2SO_4 (98%, 90 mL) was continuously stirred for 2 hrs in a 1000 mL volumetric flask at ~6 ºC in an ice bath. Then, carefully 12 g of potassium permanganate was added in a controlled manner to the suspension, preserving the reaction temperature lower than 14 ºC. The volumetric flask was removed from the ice bath and the mixture was again stirred at 35 ºC. The mixture became brownish paste after stirring for 2 h and then added 200 mL water slowly to weaken the mixture. The reaction temperature was increased quickly to 98 ºC resulted in brown colour. Finally, 40 mL H_2O_2 was added to terminate the reaction and the colour of the mixture turned yellow. The mixture was then washed by centrifugation and rinsing with 8% HCl and deionized water for several times for purification. The mixture was filtered dried in hot air oven to obtain graphene oxide (GO) powder.

Synthesis of polyaniline: Toluene and aniline were mixed in 1:4 weight ratio and 0.1 M copper sulphate solution was added for polymerization. This mixture was kept for 6-8 h to obtain the precipitate. Polyaniline (PANI) was obtained by washing the precipitate with distilled water and heating at 100 ºC for 10 h. It exists in three different forms (Fig. 2) [15]. One form may dominate the other form depending on the oxidizing agent.

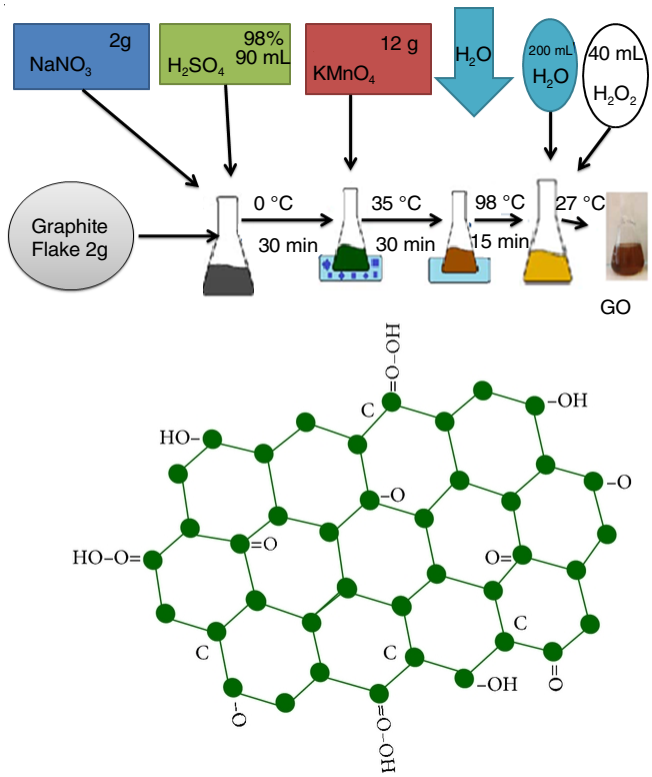

Fig. 1. Synthesis and structure of graphene oxide (GO) [Ref. 15]

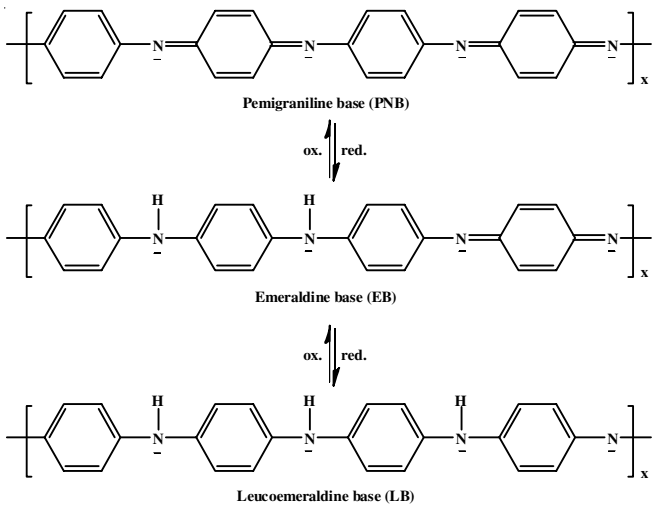

Fig. 2. Different forms of polyaniline

Fabrication of PVDF:PSSS:PVP blend membranes by solution cast method: Poly(vinylidene difluoride) (PVDF), poly(vinyl pyrrolidone) (PVP) and polystyrene sulfonic acid (PSSS) were mixed in the different ratio of 40:30:30; 50:30:20 and 60:15:25 (wt% ratio). Both PVDF (0.15 g) and PVP (0.0625 g) were mixed with 5 mL DMF in separate flask and stirred for 48 h. Then both solutions were mixed and stirred for 12 h. Poly(sodium 4-styrene sulfonate) (PSSS) was added into the blend of PVDF + PVP solution and further stirred for 48 h in order to have a uniform solution of these polymers. The viscous solution was casted in a polypropylene petridish and put in an oven at 50 ºC for 48 h, after that the PVDF:PSSS:PVP film was formed.

Preparation of ionic polymer acctuator: Firstly, 0.1g PANI was dissolved in 10 mL of DMF with continuous stirring for 24 h and then 0.09 g GO was mixed with PANI solution with continuous stirring for 48 h, to form a solution of GO/PANI. The PVDF:PSSS:PVP polymer blend membranes were dipped in viscous solution of GO/PANI for 8 h and then washed with water. This was repeated three times in order to have smooth coating of GO/PANI onto the blend membranes. Once the coating was finished, the membranes were dipped in 1.5 N LiCl solution for cation exchange process for 24 h and after that the films were taken out for further studies.

Water uptake potential: Water uptake potential (WUP) of PVDF:PSSS:PVP blend membranes was calculated by using eqn. 1:

$$WUP = \frac{W_w - W_D}{W_D} \quad (1)$$

where, W_w = Weight of wet film and W_D = Weight of dry film.

RESULTS AND DISCUSSION

The characterization of GO was performed using FTIR and Raman techniques. In FTIR, three peaks are observed in Fig. 3. The peak with lowest intensity located at 1050 cm^{-1}, which is attributed to the alkoxy C-O stretching vibration. The peak having highest intensity is observed at approximately 1730 cm^{-1} is due to the C=O stretching vibrations of a carbonyl group. The O-H stretch is also noticeable between 3500-3100 cm^{-1}.

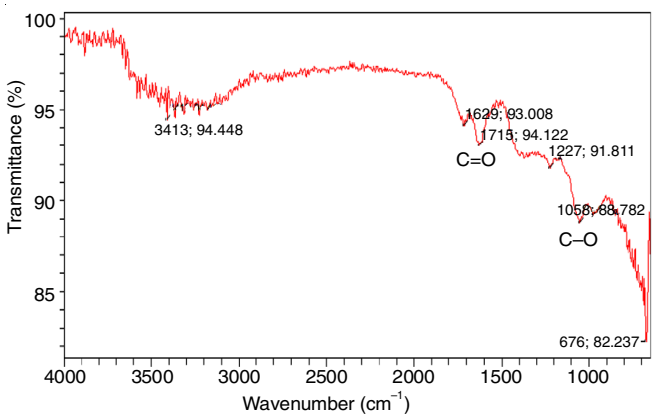

Fig. 3. FTIR spectra of GO

Two D bands were observed in the Raman spectra (Fig. 4), *viz*. D band@1352 cm^{-1} and G band@1585 cm^{-1} with I_D/I_G ratio of 0.85. Moreover, Raman spectra also indicated that GO is amorphous in nature.

Water uptake potential: As observed, water uptake potential (WUP) increases with increase of wt.% of PVDF and for the blend membrane PVDF:PSSS:PVP (60:15:25) is maximum (1.4), which is greater than the other two compositions (Table-1). It may be mentioned that for efficient actuation water uptake potential (WUP) should be nearly equal or greater than 1. Therefore PVDF:PSSS:PVP (60:15:25) blend membrane was used for studying actuation. An actuation was measured as a function of DC voltage applied to the membrane.

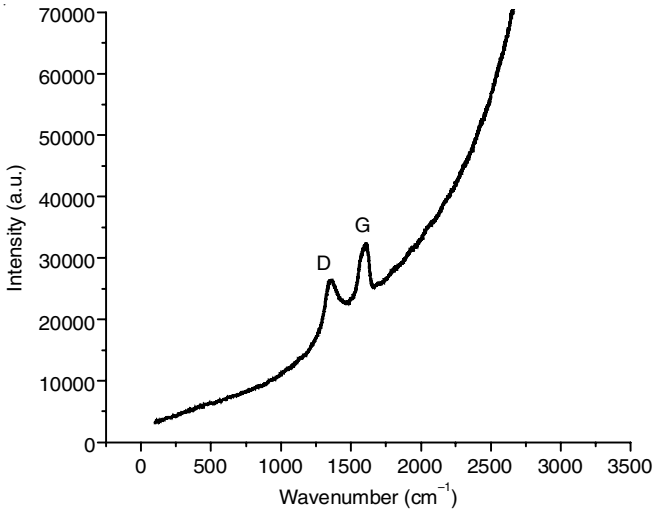

Fig. 4. Raman spectra of graphene oxide

TABLE-1
VARIATION OF WATER UPTAKE POTENTIAL AS FUNCTION COMPOSITE RATIO

System	Dry film weight (W_D, g)	Wet film weight (W_w, g)	$WUP = \frac{W_w - W_D}{W_D}$
PVDF:PSSS:PVP (40:30:30)	0.35	0.9	0.61
PVDF:PSSS:PVP (50:30:20)	0.25	0.95	0.73
PVDF:PSSS:PVP (60:15:25)	1.01	2.43	1.40

Impedance analysis: The conductivity study of the polymer electrolyte film (60:15:25) was carried out with CHI 604D electrochemical workstation. A small part of film was fixed between two stainless steel electrodes and frequency range was between 1 MHz to 1 Hz. The variation of imaginary part Z″ with the real part Z′ is shown in Fig. 5. The conductivity was calculated by eqn. 2:

$$\sigma = \frac{1}{R_b} \times \frac{l}{A} \quad (2)$$

where R_b = bulk resistance, l = thickness of thin film (0.0103 cm), A = area of the thick film (0.786 cm^2). As seen from Fig. 5, the lowest value of the bulk resistance (R_b) was found to be 200

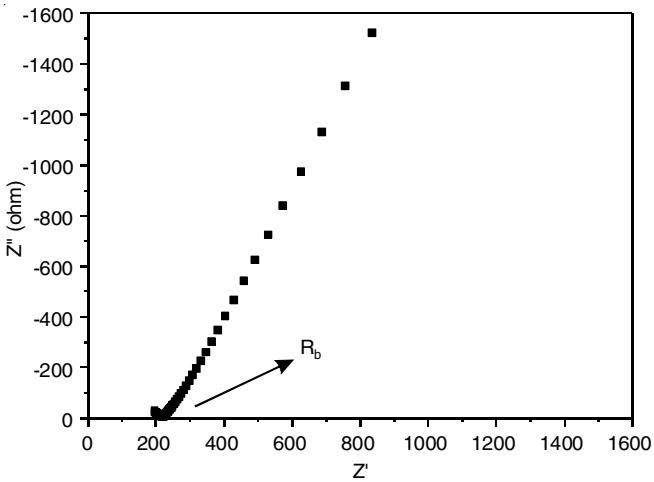

Fig. 5. Impedance of PVDF:PSSS:PVP (60:15:25)

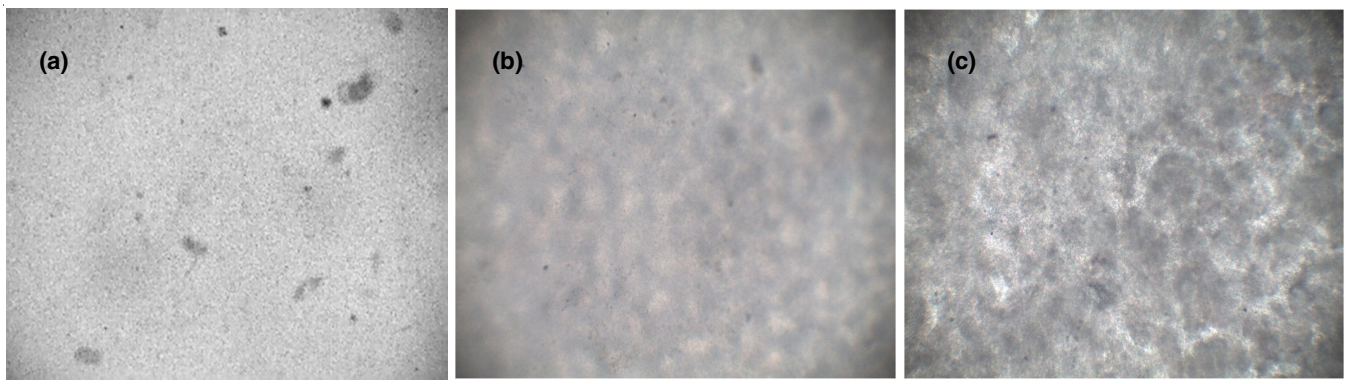

Fig. 6. Optical microscopy image of (a) PVDF:PSSS:PVP (40:30:30), (b) PVDF:PSSS:PVP (50:30:20), (c) PVDF:PSSS:PVP (60:15:25)

Ω for PVDF:PSSS:PVP. Using eqn. 2, the conductivity value was found to be 6.6×10^{-5} S/cm.

Optical microscopic study: Polarized optical micrograph (POM) of PVDF:PSSS:PVP blend membranes were recorded using Motic-BA310POL, Carlsbad, California, USA POM instrument at 40× magnification. The optical microscopic images of polymer blend membrane of the three compositions PVDF:PSSS:PVP are shown in Fig. 6. The dark region, in general, indicates amorphous nature of the polymer blend membranes. It is documented in literature [21] that with the increase in concentration of PVP, the crystallnity of PVA/PVP blends decreases thus blending with PSSS increases amorphous nature. The black portion for the composition of PVDF:PSSS:PVP (60:15:25) clearly indicates this behaviour may result in enhancing the conductivity of polymer membrane.

XRD studies: The X-Ray diffraction studies were done using Rigaku Miniflex (Cu*K*α radiation) for the PVDF:PSSS:PVP (60:15:25) blend membrane and are shown in Fig. 7. The peaks corresponding to 2θ and *h k l* values in brackets are 19 (1 0 0), 22 (0 2 0) and 39 (0 2 1). The results show the crystalline character of the prepared film.

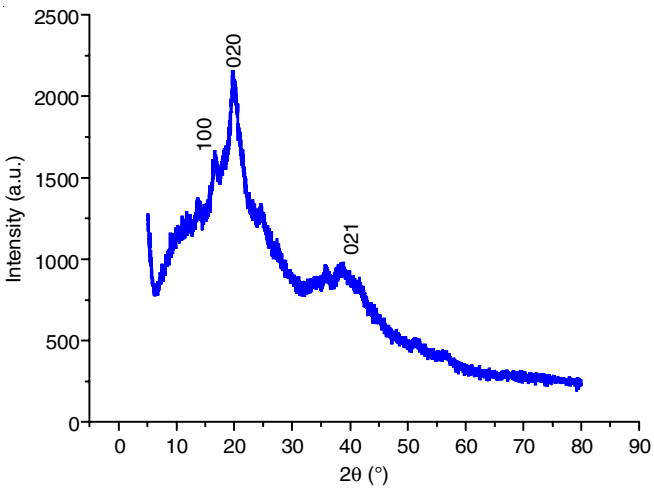

Fig. 7. XRD pattern of PVDF:PSSS:PVP (60:15:25)

Displacement graph of actuator: The actuation experiments were performed to measure the actuation of PVDF:PSSS:PVP (60:15:25) blend membrane at different time and different voltage. Fig. 8a-d show the actuation performance of the membrane. It was found that the displacement of blend membrane was 1.1 cm at 10 V. Fig. 8d shows the displacement of blend membrane for forward and reverse voltage and found that actuation is reversible.

Conclusion

Graphene oxide coated polymer blend membranes PVDF:PSSS:PVP with different compositions (40:30:30; 50:30:20 and 60:15:25 wt.%) were prepared by simple solution cast method. The blend membranes were characterized by different techniques such as XRD and optical microscope. It was found that the PVDF:PSSS:PVP with blend ratio (60:15:25) has water uptake potential of 1.4. A small displacement monitored with varying D.C. voltages and showed a maximum displace-ment of 11 cm at 10 V. A slight reverse relaxation was observed at almost all voltages. However, no back relaxation was observed. The actuator remained in that position once the voltage became stabilized. The PVDF:PSSS:PVP based IMPC actuator developed in this work may be useful for biomimetic sensors and actuators.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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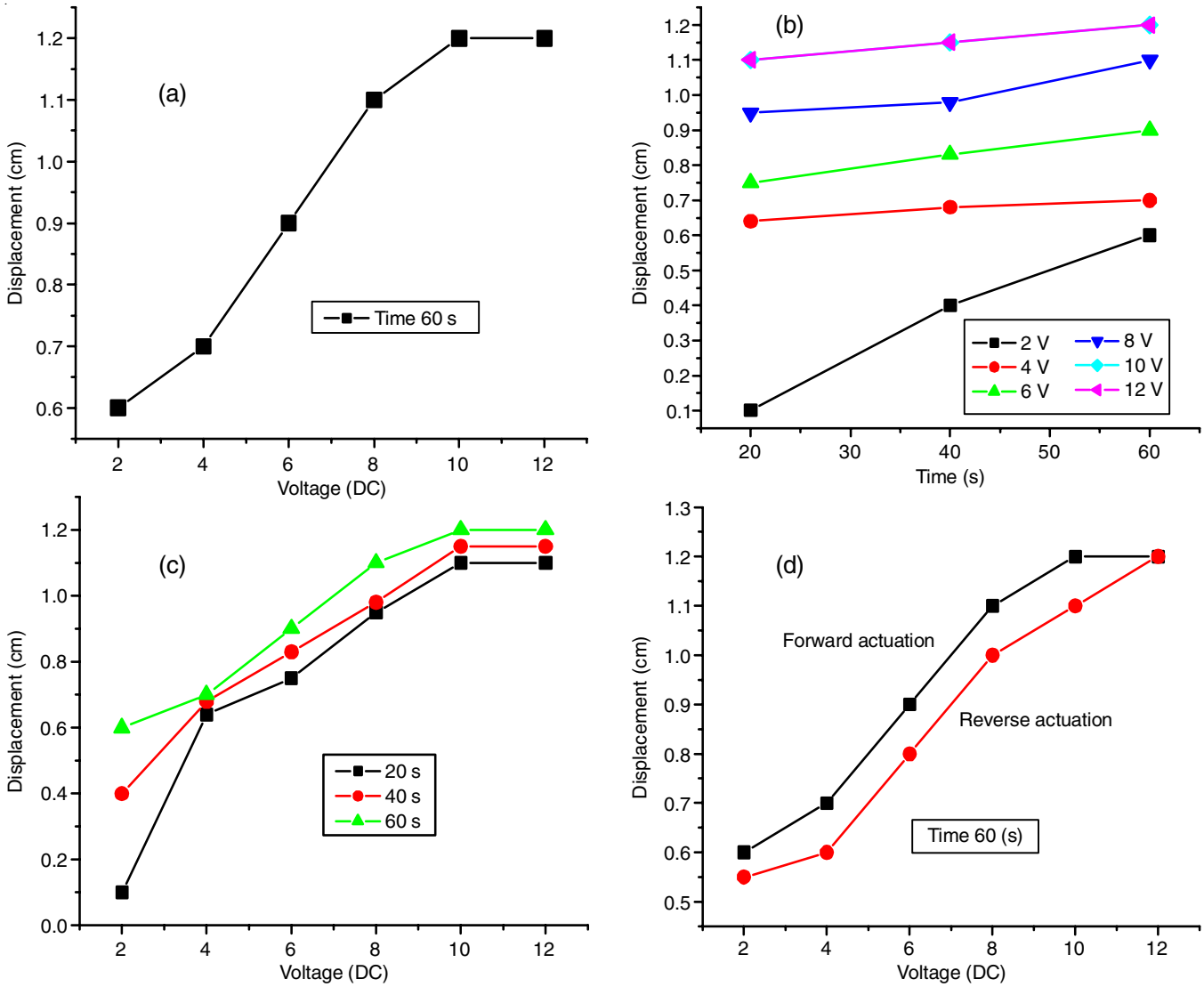

Fig. 8. Tip displacement *vs.* PVDF:PSSS:PVP (60:15:25) of (a) DC voltage, (b) time, (c) DC voltage, (d) forward and reverse DC voltage

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