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Capacitance of a solid sulfonated epoxy resin-coated electrode

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Abstract

The double layer capacitance at the interface between a cured epoxy resin and a metal was measured by cyclic voltammetry, and the a.c. technique was applied in order to access the impedance data as a measure of adhesion to the metal. Since epoxy resin is a highly insulating material, it was ionized by partially introducing a sulfonate group into the epoxy ring for electrochemical measurements. The other part of the epoxy ring was retained for making the network polymerization. The sulfonated epoxy resin cured on an interdigitated microelectrode or a parallel plate electrode pair showed reproducible voltammograms, in which current was proportional to sweep rate. Capacitance was obtained from the a.c. impedance analysis at various temperatures, and was found to be almost constant up to the glass transition temperature. In contrast, the epoxy resin mixed with Na_2SO_3 showed temperature dependence of the capacitance of Arrhenius type. When the surface was contaminated with alumina powder, its capacitance decreased drastically.

1. Introduction

Epoxy resin, which has been conventionally used for adhesive agents, film coatings, electrically insulating materials and reinforcing materials, has very strong adhesion to substrates. When the interface between the epoxy resin and the substrate is contaminated with water or organic compounds, the adhesion is blocked, probably because the contaminants open the epoxide ring to prevent the formation of the network. The physical structure of the contaminated interface can be observed through a microscope by exposing the interface by careful cutting or careful grinding of the substrate [1]. However, the exposed interface is not an adhesive interface itself but is an artificially created interface [2].

Electrochemical measurements have the potential to provide interfacial information without the use of destructive methods. They are often made in solution phase, but can be made even in an ionic solid phase by use of microelectrodes [3], if the solid phase is swollen with electrolyte [4, 5]. This swelling causes insertion of ions into the polymer to increase the ionic conductance. In order to improve the conduction, supporting electrolytes are deliberately added to polymers and/or conductive media such as poly(ethylene oxide) are used. Selection of electrolytes or media is significant in developing solid polymers for batteries and displays [6]. Unfortunately, these techniques are not suitable for the electrochemical study of epoxy adhesion, because the mixing of a supporting electrolyte or the use of conductive media drastically reduces the mechanical strength. An alternative is chemically binding the ions into the epoxy network. Since the incorporated ions lose translational motion, they do not accumulate at the interface so much. Consequently, the adhesive strength may not be decreased. The ion-incorporation is also helpful for maintaining uniform concentration distribution of ions in the polymer when in contact with aqueous solution, as in ion-incorporation for polymer-coated modified electrodes [7].

In this work, sulfonated epoxy resin was synthesized by preparing a monomer which contains a sulfonate group at one end and an epoxy group at the other. The epoxy group can participate in the polymerization to produce the ionic solid, as shown in Figure 1(a). Since the conduction is ascribed to relaxation of the terminal ion rather than an ion incorporated in the backbone, good conduction is expected for small amounts of the ion [8, 9]. In order to obtain information at the adhesive interface between the polymer and metal, capacitance is measured at various temperatures.

2. Experimental details

2.1. *Preparation*

The sulfonated epoxy resin was prepared by reacting the epoxy resin, EP-828 (Yukasieru, Tokyo) with aqueous

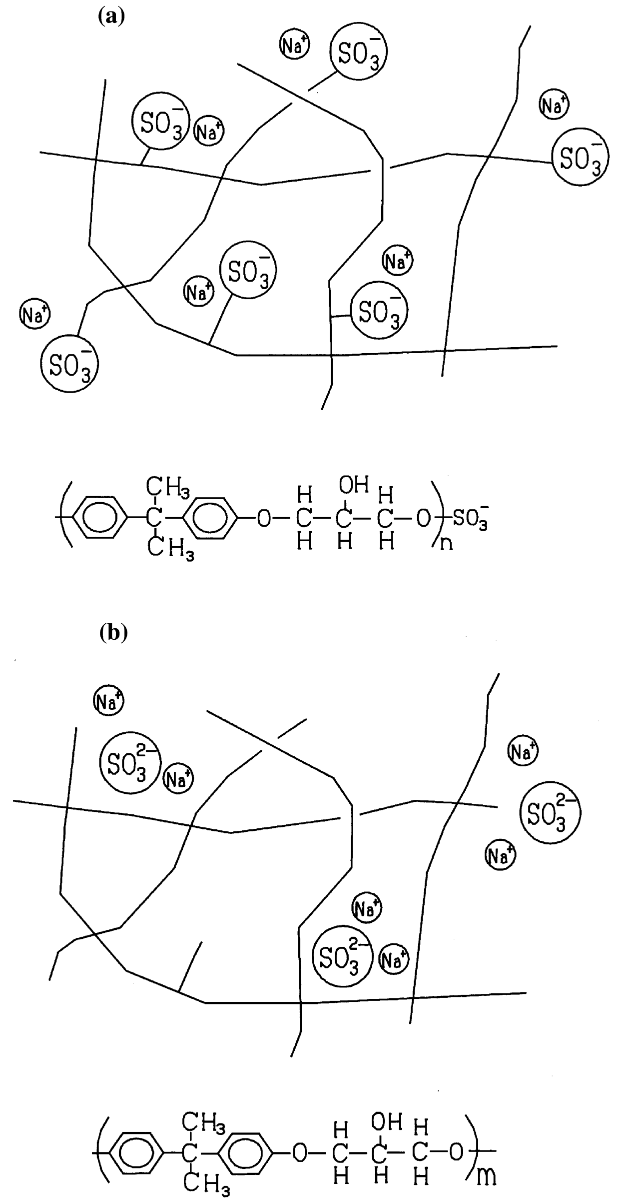

Fig. 1. Illustration of ion-distributions in the cured polymers with (a) the immobilized sulfonate ion and (b) the free sulfonate ion. Molecular structures of monomer units are shown under each ion-distribution.

$Na_2S_2O_5$ [10]. Since the yield by the documented procedure was low, we modified it so that a saturated aqueous $Na_2S_2O_5$ solution was stirred vigorously in acetone or tetrahydrofuran including an epoxy resin at least for three days in a colloidal form. Nonreacting $Na_2S_2O_5$ was removed by filtration using a 10 000 molecular weight cut-off membrane in water. The product was dried in a vacuum oven at 60 °C for 24 h. In the case of the epoxy resin + acetone mixture, some resin remained undissolved. This was removed and dried at 60 °C for one week. The degree of sulfonation was varied by varying the volume ratio of $Na_2S_2O_5$ solution:epoxy resin solution. The synthesized ion-epoxy resin was characterized by FTIR spectroscopy. Table 1 shows the assignment of some bands relevant to EP-828, $Na_2S_2O_5$ and the sulfonated EP-828. Comparison of the bands demonstrated that the sulfonate was incorporated into the epoxide and that the synthesized polymer did not include $Na_2S_2O_5$. Consequently, the resin (abbreviated as EP–SO_3Na) has structures as shown in the lower part of Figure 1. The absorbance ratios of epoxy (914 cm^{-1}):phenyl (1515 cm^{-1}) were plotted for a range of EP-828:EP–SO_3Na ratios, and this curve was then used to evaluate the sulfonate:epoxy molar ratio of the EP–SO_3Na samples.

2.2. *Polymerization*

The EP–SO_3Na was cured by mixing it with a hardener, isophthaloyl dihidrazide, which reacted with the epoxide rings that remained free from sulfonate. The curing was performed on an interdigitated microelectrode and on a twin plate electrode. Initially these were placed in an oven at 80 °C for 7 h at first and then the temperature was increased to 140 °C over 40 h, and then decreased gradually (0.5 °C min^{-1}) to room temperature, in order to avoid cracking of the electrode.

2.3. *Electrochemical measurements*

The polymer-modified electrode was mounted in a thermostated oven at temperatures ranging from 25 to 200 °C, with a heating or cooling rate of 0.5 °C min^{-1}. The oven was filled with nitrogen gas. Electrochemical measurements were made using a potentiostat, MPG-FZ-2501-A1 (Nikko Keisoku, Atsugi) and a lock-in amplifier, model 5210 (EG&G Instrument) using a two-electrode system. The potential scan rate ranged from 0.1 to 1.0 V s^{-1}. The potential in the voltammograms was calibrated by the redox reaction of ferrocene mixed with the EP–SO_3Na. The a.c. measurements were carried out with an amplitude of 2 V without any offset voltage, and at frequencies ranging from 30 to 2000 Hz. The conductivity of the aqueous solutions was obtained using a conductometer, HEC-110 (DKK, Tokyo).

Table 1. Assignment of significant bands EP-828, $Na_2S_2O_5$ and the sulfonated EP-828 (unit in cm^{-1})

Assignment	EP-828	$Na_2S_2O_5$	Sulfonated EP-828
Phenyl ring	1607, 1581, 1510	–	1607, 1581, 1510
Aromatic esters	1246, 1036	–	1246, 1036
Epoxide ring	914, 771	–	914, 771
$S_2O_5^{2-}$	–	1148, 1057, 976	–
SO_3^{2-}	–	995, 621, 496	–
R-SO_3^-	–	–	1145, 1035, 737, 629

The interdigitated electrode was composed of 100 platinum bands each 2 μm wide and 0.5 mm long with a 2 μm gap between the closest bands. The twin microelectrode had a $4 \times 2\,\mu m^2$ rectangular platinum working electrode and a 1×2 mm^2 rectangular counter platinum electrode with a separation of 0.5 mm. These electrodes were supplied by NTT Research Laboratory.

3. Results and discussion

To examine whether the EP–SO_3Na retains ionic conduction, the conductance was measured in a colloidal suspension at temperatures ranging from 5 °C to 100 °C. When the resin with 8% ratio of [SO_3^-]/[O of esters] was suspended in water (3 μS cm^{-1}) at concentration 0.26 wt%, the conductivity was 0.01 mS cm^{-1} at 5 °C and 1.4 mS cm^{-1} at 80 °C.

Figure 2 shows typical cyclic voltammograms of the cured poly-EP–SO_3Na at an interdigitated electrode in the presence of ferrocene, where one group of electrodes was regarded as the working electrode and the other as the counter electrode, as shown in Figure 3. Anodic and cathodic peaks appeared at about 0.1 and −0.1 V, respectively. No peak was found without ferrocene. The net potential shift due to ohmic drop is $0.2–0.06 = 0.14$ V, which was caused by the current of 0.1 μA. Thus the resistance was about 1.4 MΩ. The current value without ferrocene at $E = 0$, V was proportional to the sweep rate (Figure 4), indicating the contribution of a capacitive component, probably due to the double layer. To examine whether the capacitance was caused by the interface between the polymer and the electrode or by the bulk polymer itself, we measured the currents at electrodes with various distances between working and counter, ranging from 2 to 500 μm. Values of the current were independent of the distance, indicating an interfacial capacitive current, as illustrated in Figure 3.

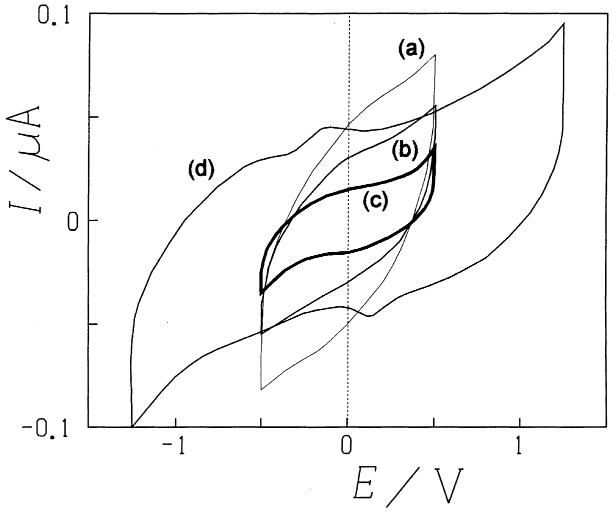

Fig. 2. Cyclic voltammograms at the interdigitated electrode of the cured poly–EP–SO_3Na without ferrocene at sweep rates of (a) 0.5, (b) 0.25 and (c) 0.1 V s^{-1} and with 0.8 wt% of ferrocene (d) at sweep rate of 0.3 V s^{-1}. Cured polymer contains SO_3^- of [SO_3^-]/[O of esters] = 0.08.

Since the current was ascribed to the charging process, we used the a.c. technique, which is more convenient than the potential sweep technique. The capacitance was evaluated by the application of 1 kHz ac voltage (amplitude 2 V) at various concentrations and temperature by use of the twin electrodes. Variation of the frequency did not provide useful information in the context of the present work. Figure 5 shows variation of the capacitance with temperature for some concentrations of poly–EP–SO_3Na. Values of the capacitance were mostly independent of temperature except at high concentration of poly-EP–SO_3Na. However, they increased slightly with increase in temperature above 140 °C. The DSC measurement showed that a transition occurred at this temperature. Since the glass transition temperature of

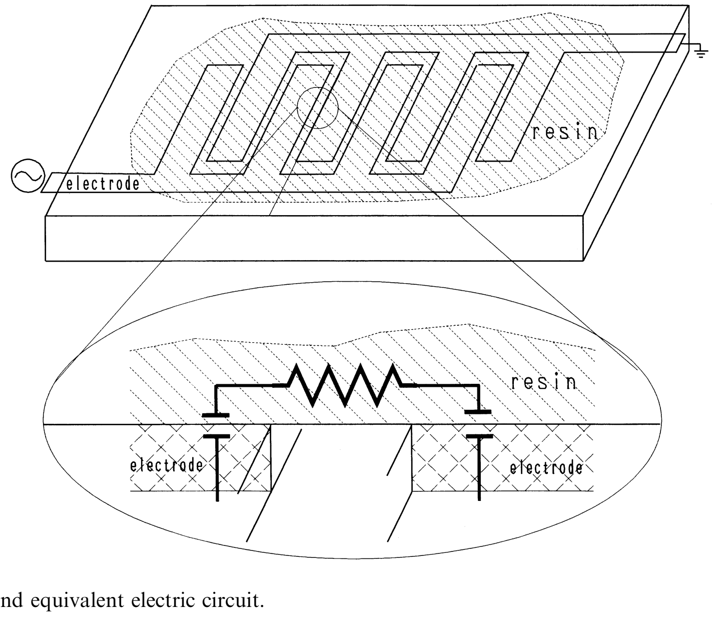

Fig. 3. Electrode arrangement and equivalent electric circuit.

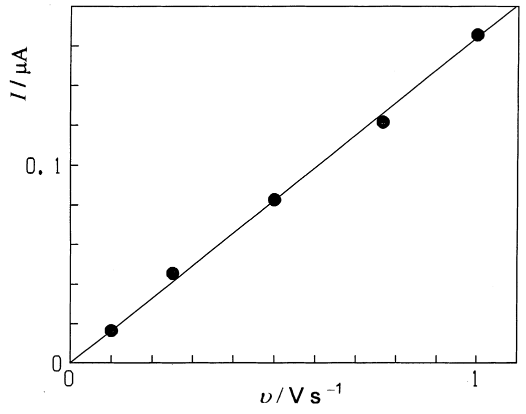

Fig. 4. Dependence of the voltammetric current at $E = 0$ of poly–EP–SO$_3$Na on potential sweep rate at 70 °C. Ionic polymer contains SO$_3^-$ of [SO$_3^-$]/[O of esters] = 0.08.

cured epoxy polymers is typically 120 °C [11], the temperature of 140 °C can be regarded as a glass transition temperature. Although the capacitance increased with concentration of the sulfonate, there was no simple relationship, especially at high concentrations of poly-EP–SO$_3$Na. Complication by ion concentration has been found even in soft polymer electrolytes such as PEO–LiClO$_4$ [12] and poly(propylene glycol)–AgCF$_3$SO$_3$ [13].

To understand the difference between the role of the immobilized sulfonate and that of the free sulfonate, we obtained the temperature-dependence of the capacitance of cured epoxy resin (Figure 1(b)) with which Na$_2$SO$_3$ was mixed without chemical bonding. The logarithm of the capacitance had a linear relation with the inverse absolute temperature (Figure 6), resembling the Arrhenius relation or Vogel–Tamman–Fulcher equation [14] for ionic polymer conduction. The logarithmic dependence can also be seen in the variation for EP–SO$_3$Na at temperatures over 140 °C in Figure 6. Since micro-Brownian motion is appreciable at temperatures above the glass transition temperature, the temperature dependence in this domain should be similar to the behaviour of the cured epoxy resin with the unbound ion [12]. In contrast, the ions of EP–SO$_3$Na at temperatures less than 140 °C can be regarded as frozen in the polymer network. The capacitance at high concentrations behaved as an Arrhenius type as in Figure 6, probably because the polymer included NaSO$_3$–EP–SO$_3$Na (both ends are sulfonated), which does not participate in the network formation.

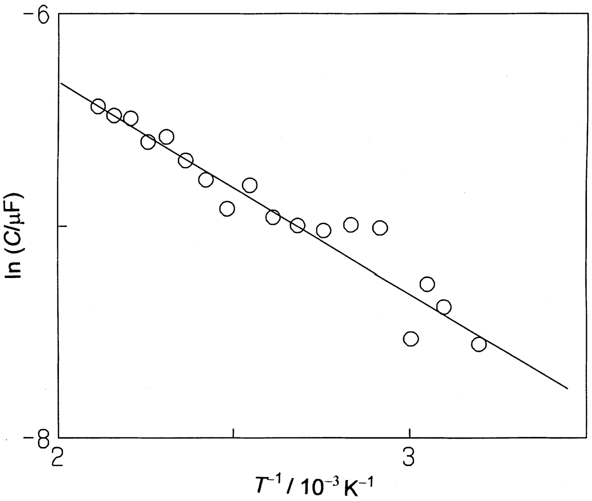

Fig. 6. Variation of logarithmic capacitance of the cured epoxy resin including Na$_2$SO$_3$.

There may be a relationship between the capacitance and contaminants on the surface to which the epoxy resin is cured. We deliberately contaminated the surface with a colloidal suspension of alumina powder as follows: an aqueous suspension of a given concentration of alumina powder was dropped on the ITO electrode and was dried; EP–SO$_3$Na + hardener was sandwiched between the two alumina-coated ITO electrodes so that the electrode separation was 0.15 mm. Figure 7 shows the variation of capacitance with the concentration of alumina. As readily predicted, the capacitance decreased with increase in the alumina concentration. The capacitance varied drastically even at the smallest concentration (0.1%). The adhesion was, however, still rather strong because the EP–SO$_3$Na could be anchored on the ITO through the interspaces among the alumina particles.

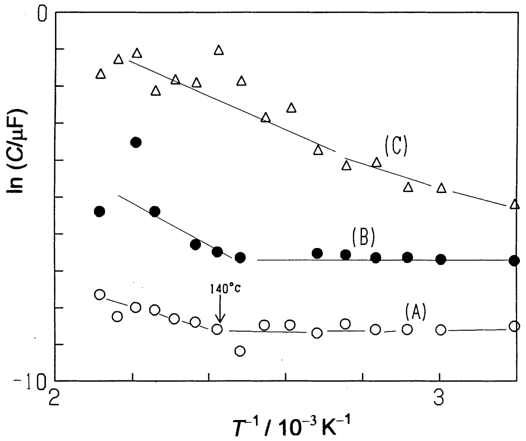

Fig. 5. Temperature dependence of the capacitance of poly–EP–SO$_3$ Na for [SO$_3^-$]/[O of esters] = (A) 0.0045, (B) 0.0085, and (C) 0.0175.

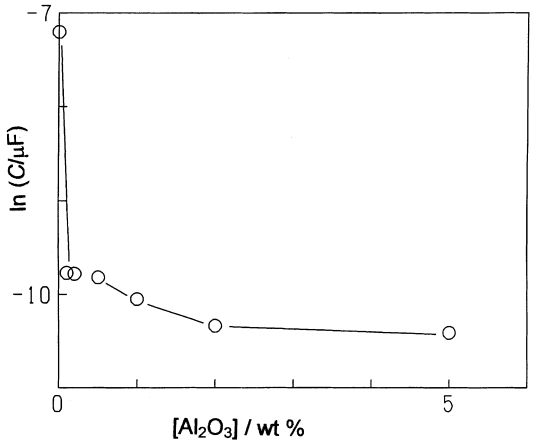

Fig. 7. Dependence of the capacitance on the concentration of the colloidal suspension of alumina.

4. Conclusion

An epoxy resin was sulfonated by replacement of one terminal epoxide ring from the monomer. It was cured to become a conducting network by the reaction of the remaining epoxide ring with isophthaloyl dihidrazide. The voltammetric response was capacitive, from which the double layer capacitance could be evaluated at various temperatures. The capacitance was mostly independent of temperature, suggesting strong immobilization of the sulfonate in the network. This was different from the behavior of a physical mixture of the epoxy resin with the salt. Therefore, the electrochemical response of the sulfonate is a measure of the structure of the network at the interface. In other words, the present technique may be a way of monitoring the interface between a metal and adhesive agents.

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