Electrical Conductivity of Poly(ethylene terephthalate) Modified by Titanium Plasma

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ABSTRACT: Ion-implantation-induced electrical conductivity in a polymer surface is known to have a different mechanism from that of metals and semiconductors. We used a technique called plasma immersion ion implantation and deposition and combined it with a titanium cathodic vacuum arc to modify the surface electrical conductivity of poly(ethylene terephthalate) (PET). The conductivity curve as a function of temperature well fitted the Mott hopping model, which has been proposed for many disordered systems. In addition, we also observed conductivity degradation when modified PET was kept at room temperature. The degradation showed a quasi-exponential decay as a function of time, that is, an aging effect, which has been seldom reported in the literature to the best of our knowledge. This could have resulted from the unusual structure of PET's surface after ion implantation. A new formula for electrical conductivity in modified PET is proposed that considers both temperature and aging effects. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3332–3336, 2008

Key words: conducting polymers; crystallization; irradiation; nanocomposites; polyesters

INTRODUCTION

Studies on the direct-current electrical conductivity of disordered systems, especially conductive materials dispersed in nonconductive networks, have been extensively performed in the past years.[1–4] The electrical conductivity of such systems shows properties different from those of metals and semiconductors, and the main mechanism for electron transport is variable-range hopping with the Efros–Shklovskii (ES) model in a low-concentration and low-temperature regime and with the Mott model in a high-concentration and high-temperature regime.[1] For both models, the conductivity can be expressed as follows:

$$\sigma = A \exp\left(-\left(\frac{T_0}{T}\right)^a\right) \qquad (1)$$

where σ is the electrical conductivity, A is a constant, T_0 is the characteristic temperature, T is the measurement temperature, and a is ½ for the ES model and ¼ for the Mott model.

These studies gave the inspiration for the study of ion-implantation-induced conductivity in polymers. When ions are implanted into polymers, the shallow surface region (usually tens of nanometers deep) will be altered. Ion-irradiation-related phenomena such as ion mixing, sputtering, crosslinking, chain scission, and carbonization make it difficult to thoroughly investigate the modified surface structure.[5] However, as far as electrical conductivity is concerned, experiments explicitly demonstrate that the surface region will undergo an insulator–metal transition when the implanted ion dose exceeds the percolation threshold.[6–10] The conductivity is controlled by electron hopping between conductive parts inside the nonconductive network; the conductive parts usually come from the π-bonded nanocrystalline graphite clusters formed by energetic ion irradiation, and the nonconductive network comes from crosslinked polymer chains.[7]

When metallic ions are implanted into polymers instead of gas ions, their inherent nonvolatile property makes metal atoms remain in the polymer matrices. Therefore, beside the π-bonded nanocrystalline graphite clusters, the embedded metal atoms can also contribute to the conductivity. We used a technique named plasma immersion ion implantation and deposition (PIII&D),[11] in which a high-voltage pulsed bias is applied to the substrate, to modify polymers that are immersed in the metallic plasma. There are implantations when the pulse is on and depositions when the pulse is off. The definition dur-

ing the pulse-off period can be collided into polymers by the ion bombardment in the following pulse-on period. Therefore, the whole surface will no longer be covered by a finely structured, continuous film, but instead there will be a complexity of mixed metal atoms with polymer chains.

Most plasma-modified polymers show an aging effect in contact-angle measurements.[12,13] In brief, an aging effect in a contact angle means that the contact angle gradually reverts back to its original value. The aging effect is driven by the minimization of surface free energy between the modified polymer and the surrounding media. For example, hydrophilic functional groups generated from modification will reorganize and immigrate from the surface to the bulk, and the surface energy normally shows a decrease in the polar force but not in the dispersion force.[13] To the best of our knowledge, an aging effect in electrical conductivity has been seldom reported in the literature. This could be due to poor adhesion between metal films and polymer surfaces that limits its applications in electronic engineering.

In this study, we used the PIII&D technique with a titanium cathodic vacuum arc to modify poly(ethylene terephthalate) (PET) and measure the electrical conductivity as a function of temperature and time when the temperature was kept at room temperature. We demonstrate that the Mott hopping model controls the conductivity and show that the degradation in conductivity is due to the unusual structure of PET's surface after ion implantation. Because electrical conductance is the reciprocal of resistance, we may use resistance instead of conductivity for simplicity most of the time.

EXPERIMENTAL

Our samples were prepared from pristine PET films (Goodfellow) with a thickness of 250 μm. The contacting electrodes for electrical resistance probing were made of silver paste on a PET surface with a 5-mm distance before the modification was performed. The base pressure was 1×10^{-5} Torr, and the working pressure was 1×10^{-3} Torr. Titanium plasma was generated by a filtered cathodic vacuum arc with Ar gas to sustain the arcing. The system description can be found elsewhere.[14] The operation parameters for PIII&D were a negative voltage of 10 kV, a frequency of 600 Hz, and a duty time of 20 μs. Different modification times were used to get different implantation doses.

The electrical resistance of modified PET as a function of temperature was measured with an HP 4156B precision semiconductor parameter analyzer (Santa Clara, CA) with a heating device. The data were collected in steps of 10 K increments starting at room temperature and 10 min after the temperature stabilized in each step. The electrical resistance as a function of time was measured by the standard four-point probe method (Keithley, Cleveland, OH). Contact-angle measurements (OCA20, Dataphysics, Germany) used two liquids, deionized water and diiodomethane, which have surface polar forces of 51 and 1.3 mN/m, surface dispersion forces of 21.8 and 49.5 mN/m, and total forces of 72.8 and 50.8 mN/m, respectively. Static contact angles were measured with the sessile drop method at three different surface spots, and the average values were taken. The X-ray diffraction (XRD) spectra were obtained with a Siemens (Madison, WI) D5005 X-ray diffractometer with a Cu Kα X-ray source at a 2° incident angle.

RESULTS AND DISCUSSION

The resistivity for pristine PET is greater than 10^{16} Ω cm and is beyond our measurement range, whereas the typical resistance for modified PET is measurable and is shown in Figure 1(a) as a function of temperature. There are three regions observed according to the tendency of the resistance curve. The first region is from room temperature to 350 K, in which the resistance shows quasi-exponential decay as the temperature increases. The second region is from 350 to 400 K, and the resistance is almost unchanged in this region. The third region is from 400 to 425 K, and the resistance keeps increasing. Unfortunately, at even higher temperatures, PET becomes mechanically soft, and this makes the measurement no more reliable.

We noticed that the glass-transition temperature (T_g) for PET is 348 K, which is close to the temperature point, 350 K, that divides regions 1 and 2 in Figure 1(a). It is then proposed that observation of resistance in the three regions can be related to PET's subtle structural evolution at different temperatures. At temperatures lower than T_g, PET's structure is rigid and is almost unaffected by a temperature increase. The electrical conductivity is controlled by electron hopping between conductive clusters inside nonconductive PET matrices; the conductive clusters can be both nanocrystalline graphite clusters and implanted titanium atoms. When the temperature exceeds T_g, PET's structural evolution starts. The chains become soft, and small conductive clusters are able to coalesce to form bigger ones. The hopping distance increases because of such coalescence, and the hopping rate decreases. Meanwhile, the hopping probability increases when the temperature increases. These two factors compensate each other, and therefore we observe a floating resistance, as shown in region 2 in Figure 1(a). When the temperature keeps increasing, polymer chains move and separate these conductive clusters further, making electron hopping
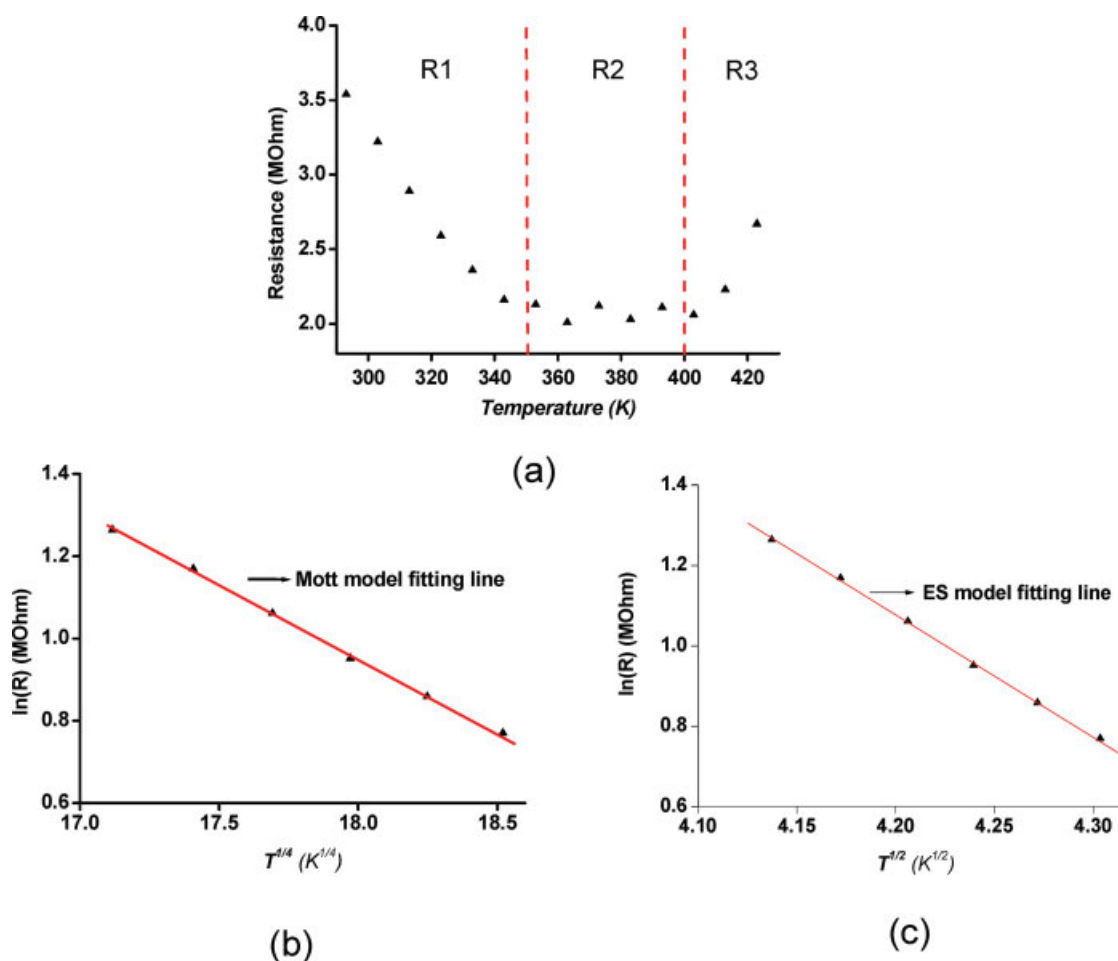
Figure 1 (a) Typical electrical resistance for modified PET as a function of temperature. There were three regions observed according to the resistance tendency. Region 1 (R1) started from room temperature and went to 350 K, region 2 (R2) started from 350 K and extended to 400 K, and region 3 (R3) started at temperatures higher than 400 K. (b,c) Linear fitting of the plot of ln R with $T^{1/2}$ and $T^{1/4}$ by adoption of the ES model and Mott model, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

more difficult. Thus, the resistance keeps increasing, as shown in region 3 in Figure 1(a).

We limited our interest to region 1 and verified the aforementioned proposition. The electron hopping model is used as the mechanism that controls the conductivity. From eq. (1), we know that a plot of ln σ with $T^{1/2}$ should be linear for the ES model and a plot of ln σ with $T^{1/4}$ should be linear for the Mott model. We observed good linear fitting lines for both models, as shown in Figure 1(b,c). However, with our experimental parameters (plasma density = 10^{10} cm^{-3}, frequency = 600 Hz, pulse duration = 20 μs, modification time = 5 min, and PET thickness = 250 μm), a simple particle-in-cell simulation gives an implantation dose of approximately 10^{16} cm^{-2}. This dose far exceeds the threshold value in percolation theory, which is normally around 10^{14}–10^{15} cm^{-2} for most ion-implanted polymers.[7] Therefore, within such a high-dose regime, the Mott model may be more suitable in describing conduction.

Figure 2(a) shows resistance measured as a function of time in hours. Resistance at time 0 means the measurement taken immediately after titanium plasma modification. We can see a sharp resistance increase with time. Such a change is similar to the aging effect in contact-angle measurements observed in many plasma-modified polymers.[13] However, for an aging effect in conductivity, few systematic studies have been performed in the past. Balakrishnan et al.[15] did notice conductivity degradation in 8 mol % yttria-stabilized zirconia (YSZ) ceramics with different microstructures at high temperatures. They found that such degradation was due to subtle displacement of oxygen ions in the 8 mol % YSZ structure. In our case, conductivity degradation is observed at room temperature, and we can suggest two possibilities here: (1) the modified PET surface tends to absorb low-energy molecules from the external environment, and this adsorption layer may degrade the conductivity, and (2) PET's surface structure can
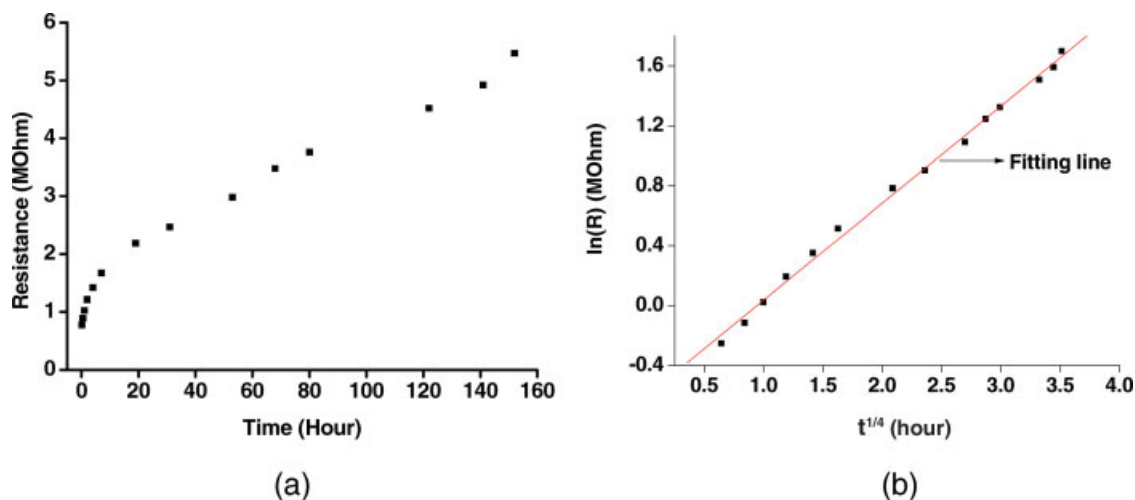
Figure 2 (a) Typical electrical resistance for modified PET as a function of time. Resistance at time 0 means that the measurement was taken immediately after modification. (b) Linear relationship observed in the aging effect for modified PET in a plot of ln R and $t^{1/4}$. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

memorize its original shape because of its excellent mechanical properties. The damaged PET chains can gradually reverse back to their original positions, and free radicals generated by ion implantation can bond to each other, crosslink PET's chains, and block electron transport.

We now evaluate the two possibilities. The adsorption layer can be characterized by contact-angle measurements. Indeed, we observed a decrease in the surface polar force from 13 to 6 mN/m but a slight decrease in the surface dispersion force from 57 to 56 mN/m. However, the adsorption layer has a thickness in the monolayer range, which is about a few nanometers, whereas the modified layer has a thickness up to 50 nm as obtained from an X-ray photoelectron spectrum depth profile and transmission electron microscopy images. The conductance occurs much deeper than this adsorption layer, and thus this adsorption layer makes electrical conductivity hardly degrade. Therefore, possibility 1 is not responsible for what we observed in conductivity.

If we consider possibility 2, crosslinking in the PET surface will make the crystallinity decrease. We measured the crystallinity with the XRD method. Figure 3 presents XRD spectra for pristine and modified PET. Only the portion for the PET peak at $2\theta = 26.08°$ is shown. The intensity of this peak is normalized to the aluminum peak at $2\theta = 38.4°$, which comes from the substrate holder (not shown). During the measurement, PET of the same size and same position was attached to the substrate holder so that the aluminum intensity is more or less constant. If the peak area is used as a comparison for different crystallinities, the ratio of modified PET to pristine PET is only about 0.2:1. Apparently, the crystallinity

is greatly reduced after the modification. Possibility 2 validates the structural evolution that is responsible for conductivity degradation.

To find out how fast conductivity ages, we assume that the resistance has an exponential rise with time. A linear fitting is then found when we plot ln R (resistance) with $t^{1/4}$, as shown in Figure 2(b). By using the Mott hopping model, we propose an equation that considers both temperature and aging effects:

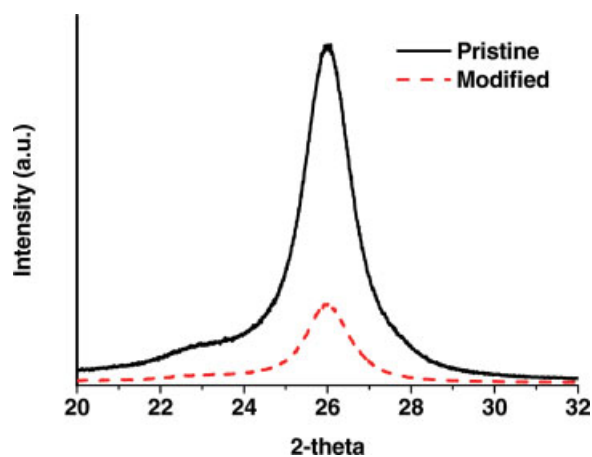$$\sigma = A \exp\left(-\left(\frac{T_0}{T} \cdot \frac{t}{t_0}\right)^{1/4}\right) \quad (2)$$

Figure 3 XRD spectra for pristine and modified PET. Only the portion of the PET peak at $2\theta = 26.08°$ is shown. The peak intensity was normalized according to the aluminum peak at $2\theta = 38.4°$ (which is not shown in this figure). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

where A, T_0, and t_0 are a constant, the characteristic temperature, and the characteristic time, respectively. t_0 is introduced here to indicate how fast the conductivity degrades.

Surprisingly, the decay coefficient for time t is also ¼, the same as the temperature coefficient in the Mott model. If we rewrite eq. (1) by replacing T_0 with the activation energy (ΔU), we obtain[3]

$$\sigma = A' \exp(-(\Delta U/kT)^a) \qquad (3)$$

where A' is constant and k is the Boltzmann constant. ΔU characterizes the energy to overcome when an electron transports from one cluster to another. We found a linear relationship between ΔU and t, that is, $\Delta U \propto t$.

CONCLUSIONS

PET was modified by titanium plasma with the PIII&D technique in our experiment. The electrical sheet conductivity was measured as a function of both temperature and time. On the one hand, three different regions were observed when the temperature was gradually increased. By consideration of high implantation in modified PET, the Mott hopping model was applied to explain the electrical conductivity in a temperature range lower than PET's T_g. For temperatures higher than T_g, the electrical conductivity was affected by subtle structural evolution and was not able to be precisely predicted. On the other hand, an aging effect in the electrical conductivity for modified PET was observed. This was proposed to be due to crosslinking happening on the PET surface, and XRD spectra revealed that PET's crystallinity was greatly reduced after modification. With time, crosslinked PET gradually blocked electron transportation between conductive clusters. We also suggested a new formula on the basis of the Mott model that considers both temperature and aging effects, and a linear relationship was found between the activation energy and time.

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