Wear Resistance of Low-Temperature Plasma-Polymerized Organosilica Deposited on Poly(ethylene terephthalate): The Effect of Discharge Powers

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ABSTRACT: An investigation was conducted into plasma polymerization of transparent organosilica (SiO_xC_y) onto flexible transparent polyethylene terephthalate (PET) substrates for improving wear resistance. The plasma-polymerized SiO_xC_y with tetramethylsilane (TMS) and oxygen (O_2) gases in room temperature (23°C) was proven to highly enhance the wear resistance from the completely worn of untreated PET substrates to no worn of TMS-oxygen plasma-polymerized PET substrates at higher discharge powers, while the wear test of 300 cycles at 300 g loading with a steel wool was applied. The performance of wear resistance on PET substrates was found to be strongly dependent on the surface characteristics of PET substrates. The surface hardness of PET substrates was determined by the pencil test. The surface morphology of PET substrate was observed by atomic force microscopy (AFM). The atomic compositions and chemical bondings of TMS-oxygen plasma-polymerized organosilicas were analyzed by means of X-ray photoelectron spectroscopy (XPS). © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2704–2710, 2008

Key words: wear resistance; PET substrates; AFM; XPS; FESEM

INTRODUCTION

Transparent polymers have been widely used for several industrial applications because of some important advantages such as low-specific weight, low-cost, and ease of design. However, their use is limited because of their poor wear resistance. These limits can be overcome by coating the polymers with hard coatings by either transparent inorganic–organic hybrid composites with covalent links between the inorganic (SiO_2 and Al_2O_3) and the organic networks (reactive dilutes and coupling agents) or transparent inorganic coatings of silicon oxides SiO_2,[1–3] SiO_xN_y,[4] and aluminum oxide (Al_2O_3).[5] The transparent inorganic–organic hybrid composites are generally prepared by the sol–gel method.[6–18] The transparent inorganic coatings are mostly deposited onto polymers by physical vapor deposition (PVD) methods of evaporation or sputtering. A pretreatment on the surfaces of polymers is always needed prior to sol–gel hybrid composites or PVD coatings deposited onto the surfaces of polymers because their adhesion to polymers is generally not as well as the adhesion of plasma enhanced chemical vapor deposition (PECVD) coatings to polymers. PECVD becomes a suitable technique for providing wear resistance coatings on polymers, while a pretreatment process on the surface of polymer prior to the PECVD coatings applied onto the surface of polymer is not essential. In this study, plasma polymerization, a special PECVD process with an organic precursor tetramethylsilane (TMS) and oxygen gas, is used to deposit antiwear organosilicas (SiO_xC_y) onto a transparent polymer polyethylene terephthalate (PET) for enhancing wear resistance.

SiO_xC_y coatings formed onto substrate by plasma polymerization of organic precursors with O_2, providing a quite different coating mechanism from PECVD of inorganic precursor silane (SiH_4) with either O_2, nitrous oxide (N_2O) or carbon dioxide (CO_2). SiO_2 with PECVD is produced onto substrate by reduction–oxidation (redox) reacting an inorganic precursor SiH_4 with either O_2, N_2O, or CO_2, at substrate temperatures between 200 and 400°C. SiO_xC_y with plasma polymerization is deposited onto substrate by the step growth mechanism of active species in organic precursor dimethylsiloxane (DMSO) or tetramethylorthosilicate (TMOS) with O_2 onto the surface of substrate, at room temperature (23°C).[1,2,19] Therefore, plasma polymerization, a process that results in the preparation of a new type of material and is not a kind of traditional polymerization, prepares a new type of materials that is very different

from conventional polymers and are also different from most inorganic materials.

Organic precursors DMSO,[1] TMOS,[2] and HMDSO[3] containing oxygen and silicon have been used to deposit SiO_xC_y on polymers for enhancing the surface hardness of transparent polymers, polycarbonate (PC) and polymethyl-methacrylate (PMMA). Benitez et al.[1] proved the plasma-polymerized coating on PC with DMSO monomer can improve the hardness from 170 MPa for untreated PC to 440 MPa for DMSO plasma-polymerized PC as measured by the nanoindentation technique. Yang et al.[2] proposed the plasma-polymerized coating on PMMA with TMOS monomer can improve the hardness from 2H for untreated PMMA to 6H for TMOS plasma-polymerized PMMA as measured by pencil test. Barrell et al.[3] claimed the plasma-polymerized coating on PC with HMDSO monomer can improve the hardness from 1.2 GPa for untreated PC to 12 GPa for HMDSO plasma-polymerized PC illustrated by Young's modulus measurement. In this study, an organic precursor TMS containing silicon was attempted to be fed in plasma chamber with oxygen gases in room temperature (23°C) to deposit an anti-wear coating organosilica (SiO_xC_y) onto PET substrate. This work presents how the wear resistance of PET substrate enhanced by TMS-O_2 plasma-polymerized organosilica using various discharge powers and affected by the surface properties of TMS-O_2 plasma-polymerized PET and the film properties of TMS-O_2 plasma-polymerized SiO_xC_y.

EXPERIMENTAL

Plasma polymerized organosilica

TMS (99% pure) and oxygen gases (99.9% pure) were fed into in a low-temperature glow discharge plasma chamber (55 cm long, 47.5 cm wide, 19.5 cm high) for deposition of plasma-polymerized SiO_xC_y coatings on a 125-mm thick PET substrate (Dupont Teijin PET substrate-SL) at TMS of 3 sccm and oxygen flow rate of 12 sccm. Other plasma settings were adjusted as shown in Table I. The pressure of the reactor chamber is decreased to less than 5 mTorr with a pressure leak rate of less than 0.1 mTorr/min, i.e., the leak flow rate of air in the chamber is less than 1% of the flow rate of the inlet gases. When the chamber pressure stabilizes, radio frequency (RF) discharge power is applied to create the TMS and oxygen plasmas. After plasma polymerization, the RF discharge power is turned off. Gases are pumped out and system pressure returned to background pressure (around 5 mTorr). The vacuum is broken by opening a valve to admit air into the chamber. Once the chamber pressure reaches atmospheric

TABLE I
The Settings of TMS-O_2 Plasma-Polymerized SiO_xC_y on PET Substrates

Parameters	Settings
Discharge power	100, 150, 200, and 250 W
Chamber pressure	60 mTorr
TMS flow rate	3 sccm
Oxygen flow rate	12 sccm
Duration	90 min

pressure (typically within 5 min), the plasma-polymerized PET is taken out for further testing.

Wear resistance test

The surface of PET substrate worn by a steel wool of 0000 grade for 300 cycles at 300 g loading was used to describe the wear resistance of PET substrate. The transmittance (at 550 nm) reduced on the worn area was recorded as the wear loss ($\Delta T\%$) of PET substrate dependent on the worn cycles. The transmittance of PET was measured by a UV–visible spectroscope of Labguide DH2000-BAL. ΔT (%) is calculated by eq. (1). $T_{unscratched}$ is the transmittance of the specimen before worn. $T_{scratched}$ is the transmittance of the specimen after worn for certain cycles.

$$\Delta T(\%) = T_{unscratched}(\%) - T_{scratched}(\%) \qquad (1)$$

Pencil test

The surface hardness of PET substrate was determined by the pencil test according to the standard method ASTM 3363. The pencils with hardness from 3H to 7H were used to wear on the surfaces of PET substrates at an angle of 45°. No wear on the surfaces of PET substrates was recorded as the surface hardness.

Surface morphology observed by AFM

The surface morphology of PET substrate was determined by Atomic force microscopy (AFM). AFM data is collected on a Veeco Instruments-Dimension 3100 apparatus with a system Nanoscope 4. A taping mode with force constant of 40 N/m, operation voltage of 0.6–0.7 V, engagement ratio of 1, and frequency of 325 kHz was applied through the tip of silicon nitride for scanning the sample surfaces. The roughness of PET substrate determined with the AFM was analyzed using a computer. Two parameters, the mean square root of roughness (R_{ms}) and

the average roughness (R_a) were calculated by the eqs. (2) and (3).

$$R_{ms} = \sqrt{\frac{\sum_{n=1}^{N}(Z_n - \bar{Z})^2}{N-1}} \quad (2)$$

$$R_a = \frac{\sum_{n=1}^{N}|Z_n - Z|}{N} \quad (3)$$

R_{ms} represents the roughness of the standard deviation from the height mean. R_a represents the roughness of the mean deviation from height mean.

XPS analysis

X-ray photoelectron spectroscopy (XPS) data are collected in both survey and high resolution modes on a Thermo VG Scuentific-Sigma Probe and the system is equipped with an Al Kα X-ray source at 1486.6 eV as XPS has a high resolution for carbon, oxygen, and silicon. Data are recorded at a 53° collecting angle, while high resolution spectra had a spot size of 400 μm resulting in analysis depths of ∼ 5 nm.

FESEM

The thickness of plasma-polymerized organosilica was evaluated with field emitted scanning electron microscopy (FESEM) by measuring the thickness on the cross section of the specimens. FESEM was collected on a HITACHI S-4800 and system equipped with an electron gun emitted by a cold field with a electrical voltage of 1 kV and an electrical current of 5 μA. Data were recorded at a scan area of 500 nm and pixels of 1024 × 840.

RESULTS AND DISCUSSION

Wear resistance of PET substrate

Untreated PET substrate shows a poor wear since the wear loss of 50% is shown in Figure 1 for 50 cycles at 300 g loading. For further worn 300 cycles, a severe wear loss of 100% was observed. A wear resistant coating is needed for PET substrates. As TMS-O$_2$ plasma-polymerized SiO$_x$C$_y$ was applied onto the surface of PET substrate at discharge power 100 W, the wear resistance of PET substrate was improved, for the wear loss is reduced to be 30% for 300 cycles at 300 g loading shown in Figure 1. For higher discharge powers, 200 and 250 W were applied to deposit TMS-O$_2$ plasma-polymerized SiO$_x$C$_y$ onto the surface of PET substrate, Figure 1 shows a supreme wear resistance of PET substrate approaches as no wear loss on the surface of PET substrate was observed even for 300 cycles at 300 g
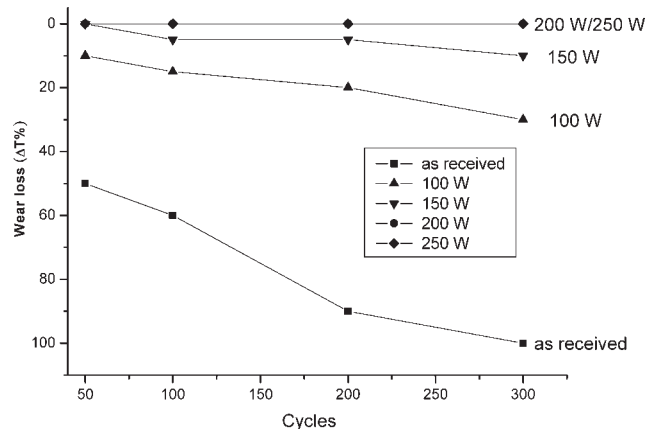

Figure 1 The wear loss (ΔT%) of untreated PET substrate and TMS-O$_2$ plasma-polymerized PET substrates at various discharge powers was plotted as a function of wear cycles at 300 g loading.

loading. The low-temperature plasma-polymerized SiO$_x$C$_y$ with TMS and oxygen gases at discharge powers 200 and 250 W in room temperature (23°C) was proven that can significantly improve the wear resistance of PET substrate.

Effect of surface morphology

The wear resistance of substrate is well-known to be dependent on the surface morphology. The smoother the surface of the substrate the better is the wear resistance. In this study, the surface morphology of PET substrates was observed by AFM. Figure 2 shows the three-dimensional AFM images of untreated PET substrate and TMS-O$_2$ plasma-polymerized PET substrate at various discharge powers. Figure 2 illustrates the surface of untreated PET substrate [Fig. 2(a)] is much rougher than the surfaces of TMS-O$_2$ plasma-polymerized PET substrates [Fig. 2(b–d)]. The surface roughness of untreated PET substrate was 0.906 nm for R_a and 0.718 nm for R_{ms}. When TMS-O$_2$ plasma-polymerized SiO$_x$C$_y$ was applied onto the surface of PET substrate at discharge power 100 W, the surface roughness of PET was greatly decreased to 0.443 nm for R_a and 0.343 nm for R_{ms}, shown in Table II. For the higher discharge powers 150–250 W were applied to deposit TMS-O$_2$ plasma-polymerized SiO$_x$C$_y$ onto the surface of PET substrate, Table II shows the less surface roughness of PET substrates, 0.156–0.263 nm for R_a and 0.124–0.208 nm for R_{ms} were observed. The higher the discharge power of plasma-polymerized SiO$_x$C$_y$, the lesser is the surface roughness of PET substrate.

Effect of surface hardness

The surface hardness of untreated PET substrate is 3H. As TMS-O$_2$ plasma-polymerized SiO$_x$C$_y$ was
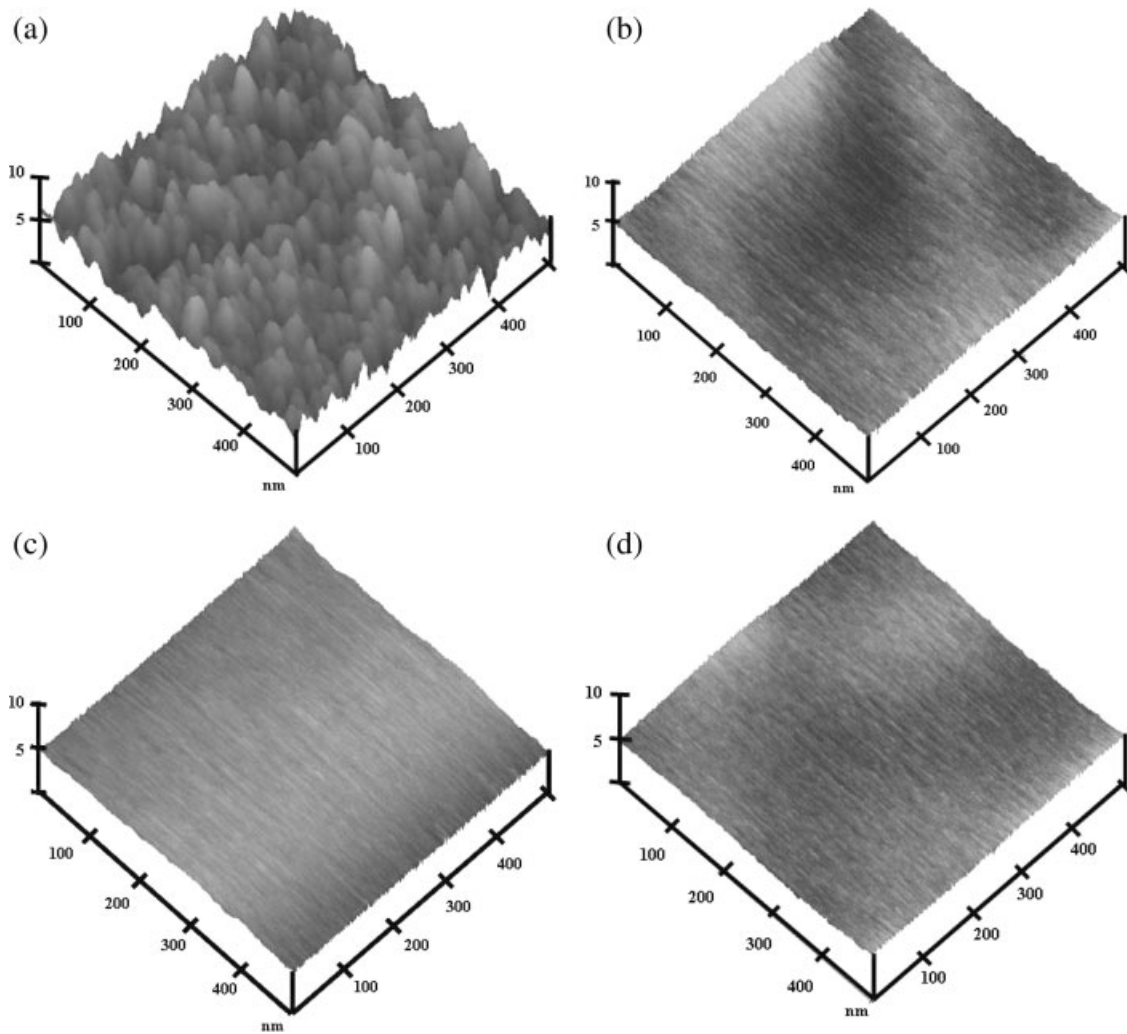
Figure 2 The three-dimensional AFM pictures of (a) untreated PET substrate and TMS-O$_2$ plasma-polymerized PET substrates at discharge powers of (b) 150 W, (c) 200 W, and (d) 250 W.

deposited on PET substrates at discharge powers of 100 and 150 W, the hardness of PET substrate can be improved to 4H as shown in Table II. When discharge powers were further increased to 200 and 250 W, the hardness of PET substrate can be further increased to 6H and 7H. The surface hardness on the surface of PET substrates was found to be critical for enhancing the wear resistance of PET substrates

by deposition with plasma-polymerized SiO$_x$C$_y$ at various discharge powers. The surface hardness of 6H on PET substrate of plasma-polymerized SiO$_x$C$_y$ at discharge powers of 200 and 250 W as shown in Table II was found to be well-enough to allow the TMS-O$_2$ plasma-polymerized PET substrate to pass the wear test by a steel wool worn 300 cycles at 300 g loading as shown in Figure 1.

TABLE II
Surface Roughness, Surface Hardness, Thickness, and Deposition Rate of Plasma-Polymerized SiO$_x$C$_y$ on PET Substrates at Various Discharge Powers

| Discharge power (watts) | Surface roughness | | Surface hardness | Thickness of plasma-polymerized SiO$_x$C$_y$ (μm) | Deposition rate of plasma-polymerized SiO$_x$C$_y$ (nm/min) |
	R_a (nm)	R_{ms} (nm)			
100	0.443	0.343	4H	0.64	7.1
150	0.263	0.208	4H	0.81	9.0
200	0.253	0.199	6H	0.90	10.0
250	0.156	0.124	7H	1.47	16.3

Effect of atomic compositions and chemical bondings

The C_{1s}, O_{1s}, and Si_{2p} spectra of untreated PET substrate and TMS-O_2 plasma-polymerized PET substrates at various discharge powers (100, 150, 200, and 250 W) were presented in Figures 3(a–c). Figure 3(a) shows the spectra of C_{1s} of PET substrate that becomes smaller. The binding energies of chemical bonds of C—C, C—O, and C=O of Si—$(R)_4$, $(R)_3$—Si—$(O)_1$, $(R)_2$—Si—$(O)_2$, and $(R)_1$—Si—$(O)_3$ were listed in Table III. Si—$(R)_4$ is the structure of TMS. $(R)_2$—Si—$(O)_2$ is the structure of PDMS (polydimethylsiloxane). $(R)_1$—Si—$(O)_3$ and $(R)_3$—Si—$(O)_1$ are the proposed chemical bonds, which are also formed onto PET, as indicated in Table III. Although TMS-O_2 plasma-polymerized SiO_xC_y is deposited onto the surfaces of PET substrates at the higher discharge powers, the less atomic composition of carbon on the surfaces of TMS-O_2 plasma-polymerized PET substrate, for 5.2%–17.5% of carbon than untreated PET substrate for 77.8% of carbon was found in Figure 4.

Figure 3(b) shows the spectra of O_{1s}, of PET substrate turn into larger when TMS-O_2 plasma-polymerized SiO_xC_y is deposited onto the surfaces of PET substrate. Although TMS-O_2 plasma-polymerized SiO_xC_y is deposited onto the surfaces of PET substrate at higher oxygen flow rates that outcome a higher atomic composition of oxygen on the surfaces of TMS-O_2 plasma-polymerized PET substrates, from 22.2% for untreated PET substrate to 47.1%–58.7% for TMS-O_2 plasma-polymerized PET substrate revealed in Figure 4. Figure 3(c) illustrates the spectra of Si_{2p} for PET substrate becomes larger, while TMS-O_2 plasma-polymerized SiO_xC_y is placed onto the surfaces of PET substrate at higher discharge powers, which results in a higher atomic composition of silicon on the surfaces of TMS-O_2 plasma-polymerized PET substrate shown in Figure 4.

The Si_{2p} spectra in Figure 3(c) was deconvoluted after substraction of the background using a Lorentzian(70%)-Gaussian (30%) function with full width at half maximum of 2 eV for interpreting the effects of silicon chemical bonds for enhancing wear resistance of PET substrates by TMS-O_2 plasma-polymerized SiO_xC_y. The binding energies of silicon chemical bonds, such as Si—$(O)_4$ at 103.4 eV, $(R)_1$—Si—$(O)_3$ at 102.8 eV, $(R)_2$—Si—$(O)_2$ at 102.1 eV, $(R)_3$—Si—$(O)_1$ at 101.5 eV, and Si—$(R)_4$ at 100.9 eV, were shown in Table III. The silicon chemical bonds of $(R)_1$—Si—$(O)_3$ and $(R)_3$—Si—$(O)_1$ were resolved from Si_{2p} peak with a method described by Alexander et al.[20]

TMS-O_2 plasma-polymerized PET substrate with an increase of discharge power from 100 to 250 W in Figure 5 outcomes an increase of the proportion of
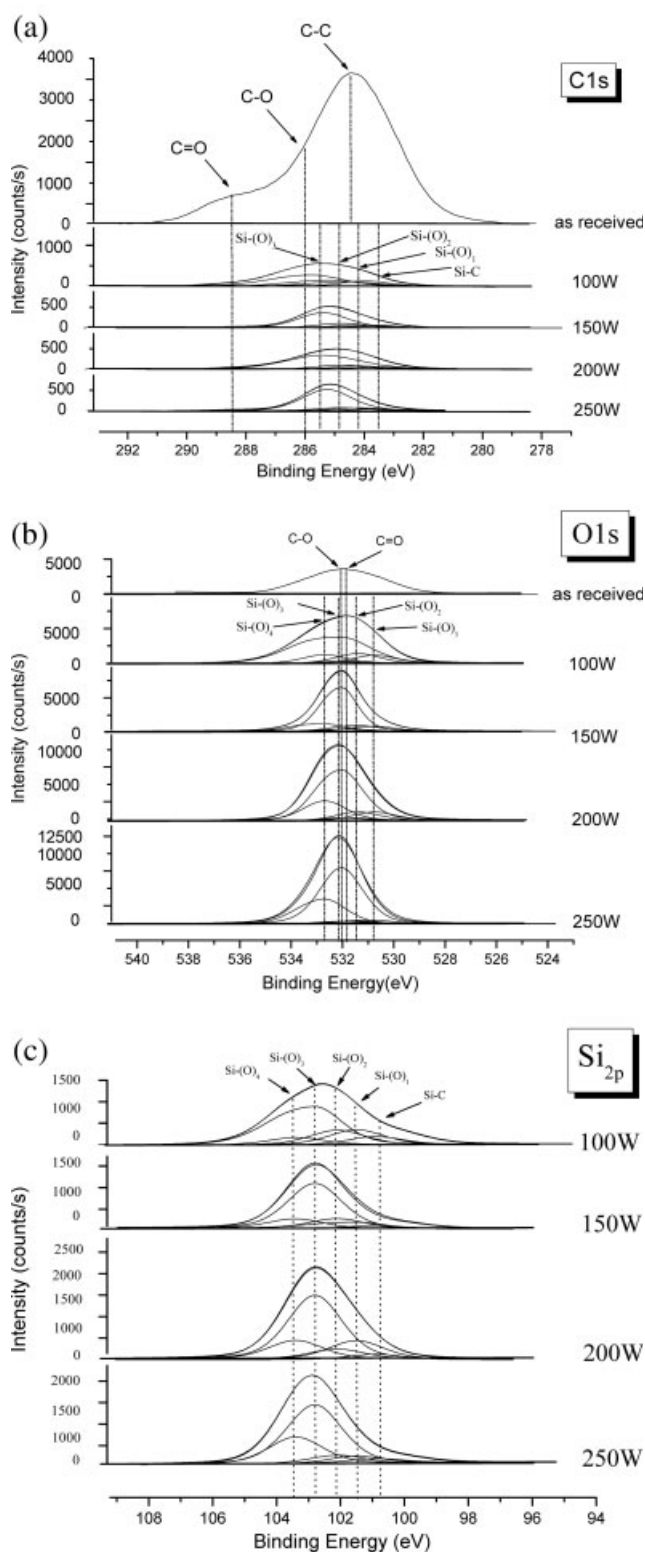

Figure 3 (a) C_{1s}, (b) O_{1s}, and (c) Si_{2p} spectra of untreated PET substrate and TMS-O_2 plasma-polymerized PET substrates at various discharge powers.

chemical bond Si—$(O)_4$ from 6.9% to 24.6% and a decrease of the proportion of chemical bonds $(R)_2$—Si—$(O)_2$, $(R)_3$—Si—$(O)_1$, and Si—$(R)_4$ from

TABLE III
The Binding Energies of Silicon Chemical Bonds on Plasma-Polymerized SiO_xC_y Corresponding XPS Spectra of C_{1s}, O_{1s}, and Si_{2p}

Structure	O | O -Si- O | O	O | R -Si- O | O	R | R -Si- O | O	R | R -Si- O | R	R | R -Si- R | R
Abbreviation	$Si-(O)_4$	$(R)_1-Si-(O)_3$	$(R)_2-Si-(O)_2$	$(R)_3-Si-(O)_1$	$Si-(R)_4$
Binding Energy (eV)					
C_{1s}	NA	285.4	284.8	284.2	283.6
O_{1s}	532.7	532.05	531.4	530.75	NA
Si_{2p}	103.4	102.8	102.1	101.5	100.9
Source	SiO_2 (Silica)	Estimate[20]	PDMS	Estimate[20]	TMS

PDMS, polydimethylsiloxane; TMS, tetramethylsilane; R, carbon and hydrogen containing structure; NA, not available.

13.9%, 14.3%, and 7.8% to 7.7%, 6.8%, and 3.7%. The proportion of chemical bond $(R)_1-Si-(O)_3$ is independent of discharge power and remains at 57%. An increase of the proportion of chemical bond $Si-(O)_4$ from 12.0% (at discharge power 150 W) to 18.2%–24.6% (at discharge power 200–250 W) for TMS-O_2 plasma-polymerized PET substrate shown in Figure 5 results in an increase of surface hardness for TMS-O_2 plasma-polymerized PET substrate from 4H to 6–7H.

When higher discharge powers, 200 and 250 W, are applied to TMS-O_2 gases, more reactive species O• and •Si• are created. Then O• reacts with reactive species •Si• and more reactive species •Si—O were formed onto the surface of PET substrate. It results in the higher proportions of chemical bond $Si-(O)_4$ for18.2% and 24.6% are found on the surface of PET

substrate, which is used to offer a hard (6–7H) surface. It offers a supreme wear resistance of TMS-O_2 plasma-polymerized PET substrate, as no wear loss was observed in Figure 1.

Effect of thickness and deposition rate of plasma-polymerized organosilicas

Table II shows the thickness of TMS-O_2 plasma-polymerized organosilica on PET substrates by discharge powers of 100, 150, 200, and 250 W was found to be 0.64, 0.81, 0.90 and 1.47 μm. When a higher discharge power was applied, the TMS-O_2 plasma-polymerized SiO_xC_y was deposited onto the surface of PET substrate with a higher deposition rate. When higher discharge powers of 200 and 250 W were applied, the TMS-O_2 plasma-polymerized SiO_xC_y
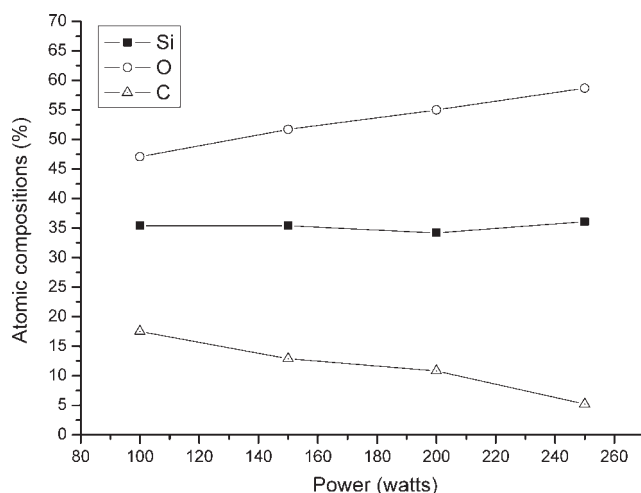

Figure 4 Atomic compositions of TMS-O_2 plasma-polymerized PET substrates were plotted as a function of discharge powers.
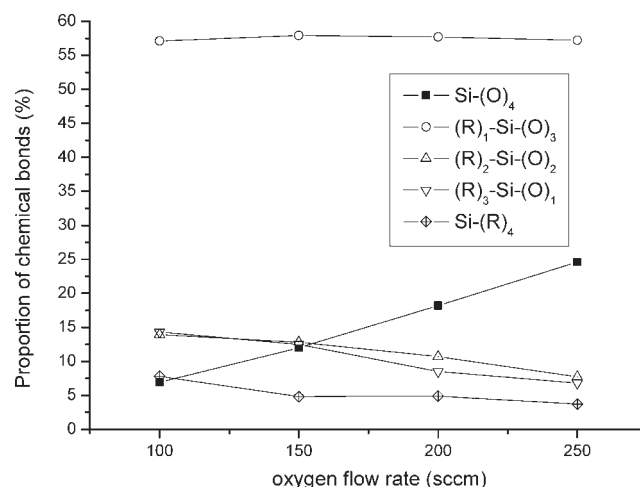

Figure 5 Proportions of silicon chemical bondings of TMS-O_2 plasma-polymerized PET substrates were plotted as a function of discharge powers.

was deposited onto the surface of PET substrate with much higher deposition rates (10.0–16.3 nm/min). Table II indicates the plasma-polymerized SiO_xC_y deposited onto PET substrate with 0.90- to 1.47-μm thick, which is thick enough to pass the wear test as no wear loss shown in Figure 1. The deposition rates of 10.0–16.3 nm/min for TMS-O_2 plasma-polymerized SiO_xC_y deposited onto PET substrates are promising, because an excellent wear resistance of TMS-O_2 plasma-polymerized PET at discharge powers of 200–250 W shown in Figure 1.

CONCLUSIONS

The wear resistance of PET substrates was proven to be greatly enhanced by the low-temperature plasma-polymerized SiO_xC_y using an organic precursor, TMS and oxygen gas at discharge powers 200 and 250 W in room temperature (23°C). No wear loss on the surface of PET substrates was observed by wearing with a steel wool for 300 cycles at 300 g loading. TMS-O_2 plasma-polymerized SiO_xC_y was used to offer a hard and smooth surface for PET substrates. The higher the discharge power of plasma-polymerized SiO_xC_y, the harder and smoother is the surface of PET substrate. While TMS-O_2 plasma-polymerized SiO_xC_y at the high discharge power of 250 W, the organosilica coatings possess 24.6% of chemical bond $Si—(O)_4$ and thickness of 1.47 μm, which results in the supreme surface hardness of 7H. Deposition rate of 16.3 nm/min of plasma-polymerized SiO_xC_y onto PET substrate results in the highly smooth surface of surface roughness at 0.156 nm of R_a and 0.124 nm of R_{ms}, respectively.

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