Preparation and Characteristics of Thin Film with Wear-Resistant Behavior on HDPE Surface Polymerized by C_2H_2–H_2–SiH_4 Plasma

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ABSTRACT: Plasma-polymerized deposition of an acetylene–hydrogen–silane mixture (C_2H_2–H_2–SiH_4) to obtain thin film with good wear behavior on a high-density polyethylene (HDPE) surface was present in this work. It was found that the bond between thin film and HDPE substrate was excellent and H_2 gas in system led the deposited thin film to better adhesive properties, but slower thin film deposition rate. Surface wear-resistant properties of modified HDPE were improved with the input of SiH_4. Infrared and X-ray photoelectron spectroscopy spectra suggested that there be large quantities of >C=O, O—H, C—Si, and Si—O groups in thin film and that the ratio of C to Si was increased due to the addition of SiH_4 and H_2, which inferred that the thin film structure and components lie between organic and inorganic materials. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1561–1566, 1998

Key words: plasma polymerization; thin film; wear resistance behavior; surface properties; adhesive strength

INTRODUCTION

Recent studies have tried to develop potential uses of plastics by means of improving material bulk properties or their surface behaviors. Plasma processing provides a way to enhance the behavior of material without changing bulk properties because only the surface is modified. The thickness of such surface modification is usually on the order of angstroms to hundreds of nanometers. There are two kinds of plasma processing, including plasma-induced polymerization (PIP) and plasma polymerization (PP). In PIP,[1] the substrate is not placed downstream from the plasma source; an inert gas, such as argon, is excited by the plasma and is convected toward the substrate. The polymerizable gas (butadiene, styrene, etc.) is mixed with the excited inert gas near the substrate and is subsequently excited to a level that initiates polymerization but does not fragment the monomer. The deposited polymer is thought to be a lightly crosslinked or noncrosslinked linear polymer with significant viscoelastic properties.[1] In PP, the substrate is placed in the glowing plasma field, and the monomer gas is fragmented by plasma and is subsequently deposited on the substrate, where it reforms into a highly crosslinked network.[2] There have been lots of

studies on plasma treatment to modify or to add chemical bonding sites to existing surface, thus providing a means to enhance adhesion to another resins and allowing for a significant increase in joint strength. Reviews pertaining to plasma processing of polymers can be found elsewhere.[3–7]

However, studies on the synthesis of wear-resistant thin film by plasma polymerization are few compared with plasma treatment to enhance surface adhesion. The most popular methods for synthesis of ultrahardness or wear-resistant thin film is chemical vapor deposition,[8,9] but its high reactive temperature (greater than 900–1000°C) and its relative low deposition rate have limited its uses in field of polymer. The process of plasma polymerized thin film deposition could[5–7] greatly lower the reactive temperature with a higher deposition rate and obtain one kind of even and better bonded thin film.

This article presents our work using plasma polymerization of a C_2H_2–H_2–SiH_4 mixture monomers to obtain a thin, adherent, good, wear-resistant film material on the surface of the high-density polyethylene (HDPE) sheet under the conditions of a low reactive temperature and a high deposition rate.

EXPERIMENTAL

Materials

Acetylene was purchased from Shanyu Gas Co., Ltd. (P. R. China) without further purification. The substrate materials was made of 5200B HDPE from Qilu Petrochemical Co. Ltd., pressed in a mold under 180°C and 150 kg/cm^2 for 20 min; the purity of hydrogen was up to 99.99%, manufactured by laboratory of H_2 storage in Zhejiang University; the concentration of SiH_4 from Zhejiang University diluted with H_2 was 20%; total pressure was 35 kg/cm^2.

Experimental Processing

The reactor for plasma deposition comprised two parallel electrodes (ground and hot electrodes) made of a large flat steel plate (20 × 15 cm), radio frequency power input, and an electric capacity coupling device (see Fig. 1). Its parameters were as follows. The power for plasma was operated at 13.6 kHz and delivered between 10–100 W. The
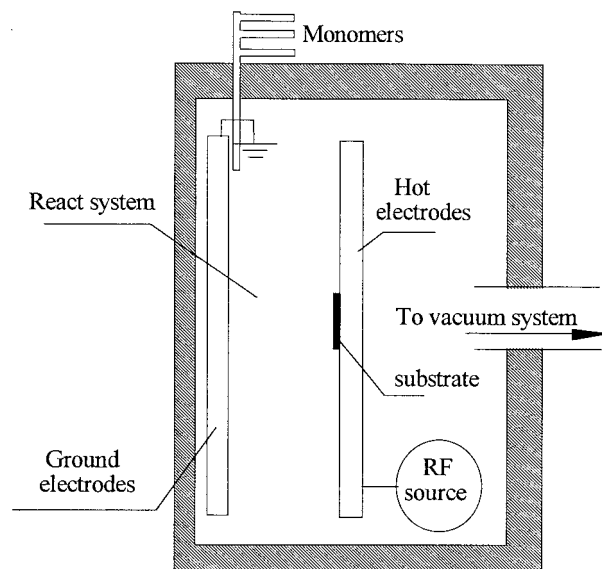

Figure 1 Schematic of the plasma polymerization reactor.

monomer flow rate was measured by a mass flow meter. The reactor chamber was first vacuumed by two mechanical pumps and then by one molecular pump to low pressure. The position of the HDPE substrate (4 × 2 × 0.2 cm) was located in the center of hot electrodes to allow a uniform distribution of thin film deposition.

Plasma processing was done in the following steps. First, the system pressure was vacuumed to 0.01 Pa, then argon gas was input to a pressure of 10 Pa so that rf power could be directed to HDPE substrate for 5-min etching of argon plasma; this step would remove surface contaminants on the substrate surface. Second, reactive monomers were input into system, and thin film was deposited on the surface of HDPE substrate for 20 min; the third step was to switch off power and monomers but reinput argon gas to the system for 20 min so as to eliminate the remainder of reactive radicals and monomers on substrate surface and system.

Thin film deposition rate was measured by a mutibeam interferometry Model 65-A5 on a slide glass substrate. The adhesive strength between the thin film and substrate was obtained by the joint of HDPE and aluminum sheet bonded with E44 epoxy (see Fig. 2). The epoxy was cured at 333 K for 2 h, and the surface of aluminum sheet was treated by W40 abrasive paper and acetone to eliminate greasy dirt and oxide on the surface. All specimens of the joint were tested in Instron-1122
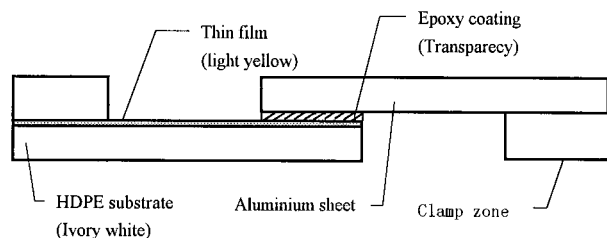
Figure 2 Schematic description of the joint between aluminium and modified HDPE.

tensile instrument at a constant crosshead speed of 10 mm/min^{-1}, 20°C, and 65% room humidity. The valid testing samples, in which more than 90% thin film was effectively separated, could be distinguished by the color contrast among the thin film (light yellow), HDPE substrate (ivory white), and epoxy coating (transparency).

The sample for abrasive test was 5 × 15 mm, on which a 4 N load with 0.4 m/s velocity covers a distance of 5.65 m. Then it was cleaned with acetone to make sure there were no particles on the surface under the observation of microscopy and then the weight loss of the abraded sample, was measured with a balance, Model Libror L-2000SM (Shimazdu Co. Ltd.) with 0.01 mg precision.

Infrared (IR) spectra of thin film scratched from slide glass surface and blended with KBr discs were recorded with a Shimazdu Co. Ltd. Model IR-479 spectrometer. X-ray photoelectron spectroscopy (XPS) spectra of deposited thin film is measured by electron spectroscopy for chemical analysis (ESCA) surface analysis produced by VG Co. Ltd. Samples scratched from a slide glass surface had been etched in Ar plasma for 10 min to eliminated O_2, N_2, and H_2O vapor on the surface.

RESULTS AND DISCUSSION

Deposition of Thin Film and Its Adhesive Behavior

Figure 3 shows the following effects of H_2 on the thin film deposition rate and its bonded behavior: the rate is rapidly down with an input of H_2, while thin film properties, including its evenness, transparency, and adhesive strength with substrate, are greatly improved since there are lots of non-polymerizable H radicals (H·), which may dilute density of polymerizable radicals (R·) and react
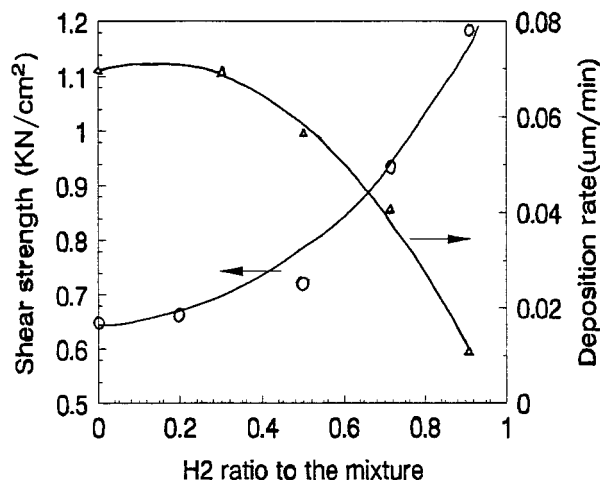

Figure 3 Effects of H_2 on film deposition rate and its adhesive behavior. Acetylene flow rate, 10 sccm; input power, 40 W; limit.

with macromolecule chains during the stage of initiation and termination to more stable deposition and severe erosion to poor adhesive particles on the substrate surface.

The SiH_4 monomer in the system also decreases the thin film deposition rate; however, there is a tendency for the deposited substance to become powder since the reaction between carbon radicals (RC·) and RSi· radicals leads to low adhesive strength between thin film and substrate (Fig. 4).
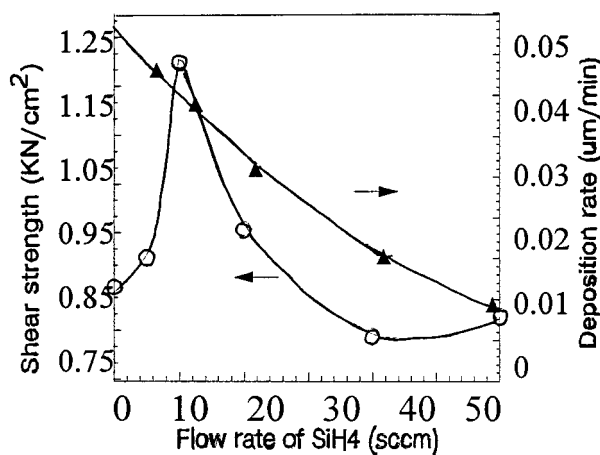

Figure 4 Effects of SiH_4 on film deposition rate and its adhesive behavior. Input power, 40 W; limited pressure; acetylene flow rate.
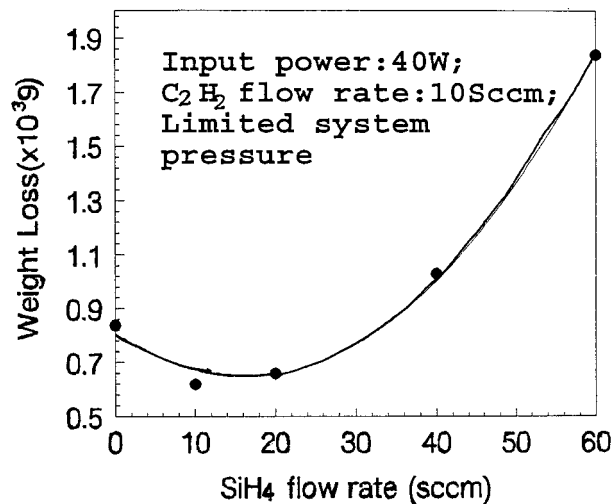
Figure 5 Effects of SiH_4 on wear properties of HDPE without adding extra H_2.

Wear-Resistant Behavior of Thin Film on HDPE Substrate

The wear-resistant behavior will become worse once the powder appears in deposited substance. The thin film in Figure 5 has large quantities of powder since the SiH_4 monomer is not further diluted by H_2. If H_2 was added in the C_2H_2–H_2–SiH_4 mixture, the whole reaction mechanism could be greatly changed, and the behavior of the deposited substance, especially its abrasive resistant behavior, was much improved. This may be because the strong erosion of the reactive H· rad-
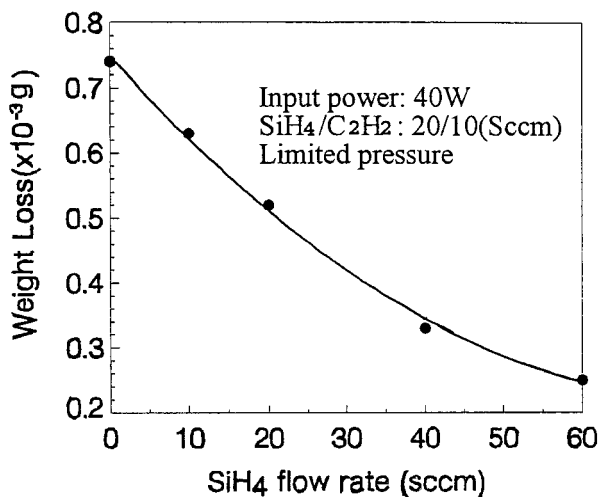

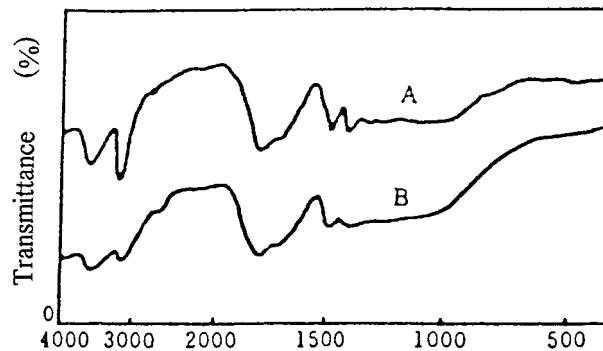**Figure 6** Effects of H_2 on wear properties of HDPE by plasma deposition.

Figure 7 Infrared spectra $(4000-400 \text{ cm}^{-1})$ of plasma polymer: (A) at 40 W, C_2H_2 (10 sccm), and 10 Pa; (B) at 40 W, C_2H_2 (10 sccm), and 10 Pa.

ical to the deposited substance leads to the growth of the inorganic component in the thin film (Fig. 6). Such phenomenon will be proved by XPS and IR spectra.

Analysis of IR and XPS Spectra

The highly branched nature is evident from the absence of strong absorption in the region of $720-770 \text{ cm}^{-1}$ characteristic of the straight chain of four or more methylene groups (Fig. 7). The hydrocarbon nature of these chains produce the C—H stretching bond near 2900 cm^{-1}; the absorption in the carbonyl region $(1665-1740 \text{ cm}^{-1})$ and the hydroxyl O—H stretch bond $(3200-3600 \text{ cm}^{-1})$ indicated the presence of the OH-group and the >C=O group; it is most possible to attribute it to the post-plasma reaction of trapped free radicals with atmospheric O_2 and/or H_2O. From curves (A) and (B) in Figure 7, the strengthening
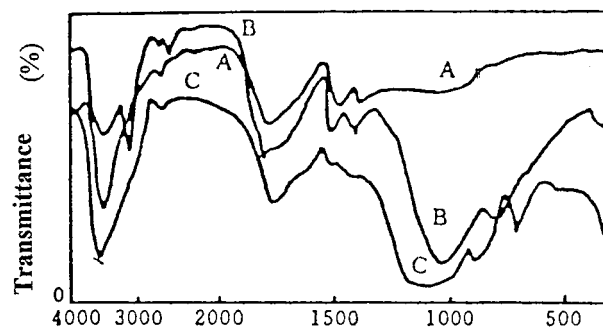

Figure 8 Infrared spectra $(4000-400 \text{ cm}^{-1})$ of plasma polymer under limited system pressure: (A) C_2H_2 (10 sccm), H_2 (10 sccm), and 10 Pa; (B) C_2H_2 (10 sccm), SiH_4 (20 sccm), and 10 Pa; (C) C_2H_2 (10 sccm), SiH_4 (20 sccm), H_2 (10 sccm), and 10 Pa.
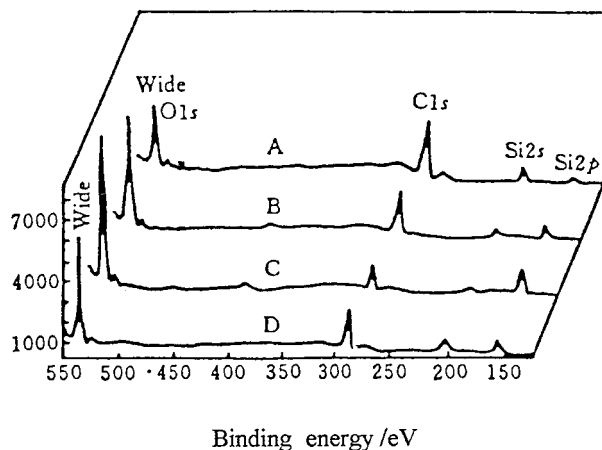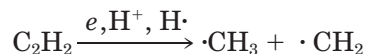
Figure 9 XPS spectra of plasma polymers of C_2H_2 and SiH_4, deposited at 40 W, limited pressure, 10 sccm C_2H_2, and other gases: (A) 40 sccm, 20% SiH_4; (B) 40 sccm, 20% SiH_4; (C) 60 sccm, 20% SiH_4; (D) 60 sccm, 20% SiH_4, and 10 sccm H_2.

of CH absorption (2952, 1445, and 1370 cm^{-1}) shows that H_2 in the plasma polymerization cause more quantities of CH_3.

In Figure 8, the stronger CH absorption (2950 and 1450 cm^{-1}) of sample (B) infers that there be more organic components than sample (C). Addition of H_2 contributes to the debonding of Si—H to an easier reaction between SiH_4 and C_2H_2 from the presence of strong twist absorption $SiCH_3$ (1250 and 800 cm^{-1}) but non-SiH absorption in 2120 cm^{-1}. Groups of Si—O—Si and Si—O—C may result from the effects of trapping radicals after they contact with atmosphere. The possible reaction of the SiH_4–H_2–C_2H_2 system are as follows.

$$n\,SiH_4 \xrightarrow{e} x \cdot SiH_3 + y \cdot SiH_2 + z \cdot SiH + m \cdot H_2$$

$$H_2 \xrightarrow{e} H^+ + H\cdot$$

$$C_2H_2 \xrightarrow{e,H^+,\,H\cdot} \cdot CH_3 + \cdot CH_2$$

$$\cdot CH_2 + \cdot SiH_3 \rightarrow CH_3 — SiH_3 \rightarrow \cdots\cdots$$

Similar results were found from XPS analysis (see Fig. 9 and Table I). Si components raised from 7.2 to 14.9% [samples (A) and (B)] or 17.1 to 21.7% after addition of H_2 gas, while the carbon concentration reduced rapidly from 59.8 to 43.0% [samples (A) and (B)] or 40.3 to 26.5% [samples (C) and (D)], respectively; all these indicate that the easy reaction between SiH_4 and C_2H_2 and the severe erosion of the H radical to organic components lead to a deposit of one kind of thin film with the structure between organic and inorganic materials.

CONCLUSIONS

C_2H_2–H_2–SiH_4 plasma-polymerized thin film was successful in improving the adhesive strength between the HDPE substrate and the deposited thin film. The bond of thin film with the HDPE surface was relatively strong, especially with addition of H_2 gas. If no extra H_2 gas was in the deposited system, silane gas (SiH_4) could easily react with C_2H_2 to cause powder substance, which would lead to poor abrasive-resistant properties of HDPE and bad adhesive behavior of thin film. Thin film without powder could be obtained, while the extra H_2 gas and silane was mixed into the react system, and its wear-resistant behavior was good compared with HDPE and the deposited substance without silane. IR and XPS analysis indicated that the H_2 and silane in the deposited system has raised the inorganic component of thin film and the ratio of carbon, and silicon of the deposited substance was up to 1.22.

Table I   C-to-Si Ratio of Thin Film Deposited Under Different Process Conditions

Sample[a]	Si/C/O/Cl	Formula	C-to-Si ratio
A	7.2/59.8/24.2/8.8	$Si_{7.2}C_{59.3}O_{24.2}Cl_{8.8}$	8.273
B	14.9/43.0/39.0/3.1	$Si_{14.9}C_{43.0}O_{39.0}Cl_{3.1}$	2.877
C	17.1/40.3/38.1/4.5	$Si_{17.1}C_{40.3}O_{38.1}Cl_{4.4}$	2.357
D	21.7/26.5/49.5/2.3	$Si_{21.7}C_{26.5}O_{49.5}Cl_{2.3}$	1.222

[a] A: Input power, 40 W; flow rate of 20% SiH_4, 40 sccm; flow rate of C_2H_2, 10 sccm. B: Power, 40 W; flow rate of 20% SiH_4, 40 sccm; C_2H_2, 10 sccm; H_2, 10 sccm. C: Power, 40 W; flow rate of 20% SiH_4, 60 sccm; flow rate of C_2H_2, 10 sccm. D: Power, 40 W; flow rate of 20% SiH_4, 60 sccm; C_2H_2, 10 sccm; H_2, 10 sccm.

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