

Preliminary Experiment of Surface Hardening of Polymers by Glow Discharge Polymerization

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Synopsis

Polymers including polyethylene, polycarbonate, and polytetrafluoroethylene were modified by glow discharge polymerization to enhance surface hardness. The surface hardness of the polymer substrates could be improved by glow discharge polymerizations of silicon-containing compounds. The mixture of tetramethylsilane (TMS) and oxygen was more effective than tetramethoxysilane to improve the surface hardness. The surface hardness improved by the glow discharge polymerization strongly depended on the nature of the polymer substrates to be modified. The adhesion between polymer films prepared from the TMS/O₂ mixture by glow discharge polymerization and the polymer substrates was good.

INTRODUCTION

Polymer substrates possess many advantages such as ease of fabrication, electrical insulation, mechanical strength, etc., but are inferior to inorganic materials such as glass and ceramics in abrasion resistance and surface hardness. When polymer substrates such as polycarbonate and poly(methyl methacrylate) are employed as optical devices, this disadvantage should be improved. To modify surface properties, many processes involving coating with organo-siloxane resins and curing are designed,¹ and some process has been commercially practiced.² Surface hardening of polyethylene is also of interest in the application of artificial articulations consisting of ultrahigh-molecular polyethylene.

Glow discharge polymerization is frequently applied for modification of polymer surfaces. The main advantages of this technique are that all processes which are required in the polymer-coating technique are accomplished by an essentially one-step process.³

This study focusses on glow discharge polymerization of silicon-containing compounds to improve the surface hardness of polymer substrates. A similar investigation has been dealt with by Wydeven⁴ using trimethylvinylsilane.

EXPERIMENTAL

Materials

Chemicals used for the glow discharge polymerization in this study were tetramethylsilane (TMS) (provided from Ventron Co.) and tetramethoxysilane (TMOS) (provided from Tokyo Kasei Co.)

Polymer substrates provided for modification by glow discharge polymerization were high-density polyethylene (PE), polycarbonate (PC) (provided from

Mitsubishi Chemical Industries), poly(methyl methacrylate) (PMMA) (from Sumitomo Chemical Co.), and polytetrafluoroethylene (PTFE) (from Nippon Asbestos Co.), and their dimension were $34 \times 240 \times 2-3$ mm. The surfaces were washed with acetone or methanol, and further with detergent, rinsed with distilled water, and then stored in a desiccator over silica gel.

Glow Discharge Polymerization

The apparatus and experimental procedures for the glow discharge polymerization are essentially the same as those reported elsewhere.⁵ The reaction chamber is a tubular reactor (35 mm inner diameter, 400 mm long) which is made of Pyrex glass, and is constructed with a monomer inlet, a pressure gauge, a vacuum system, and a matching network for inductive coupling of a 13.56 MHz radio frequency source.

The substrates were horizontally placed in the reaction chamber and the system was evacuated to approximately 0.1 mTorr using a diffusion and a rotary pump. Argon gas was introduced into the reaction chamber, and, to eliminate water adsorbed on the surfaces of the substrates, the surfaces were exposed to argon plasma for 10 min. Again the system was evacuated to 0.1 mTorr, and the monomer gas which was adjusted at the flow rate of 0.264 cm^3 (STP)/min at the pressure of 40 mTorr was injected into the reaction chamber. rf power was turned on, and the glow discharge polymerization was initiated and continued at a level of the rf power of 25 W for a suitable duration.

Surface Energy

The contact angles of the polymer films against water, glycerol, formamide, diiodomethane, and tricresyl phosphate was measured by a drop-on-plate method using a Kyowa Kagaku Contact Angle Meter CA-1. The contact angle data were analyzed to estimate a dispersive contribution γ_s^d and a polar contribution γ_s^p according to Kaelble's method.⁶

Evaluation of Adhesion between Plasma Films and Polymer Substrates

For evaluation of the adhesion between the polymer substrates and the plasma films, the Scotch tape test and lap-shear strength were designed. The *Scotch tape test* was carried out according to ASTM D-3354-76. For the measurement of *lap-shear strength*, special specimens were provided. With an aluminum coupon ($25 \times 100 \times 1$ mm) of which the surface was sandblasted, the polymer substrate was bonded using an epoxide adhesive consisting of the mixture of Epicoat 828 and Tomide 235-S at the mixing ratio of 100:70 by weight. The dimension of the overlapping part was 25×12.5 mm long. The construction of the jointing part, therefore, was a polymer substrate/plasma film/epoxide adhesive/aluminum coupon. The specimens were pressed at 5 kg/cm^2 at the temperature of 80°C for 0.5 h.

The lap-shear strength of the jointing part was measured using an Instron universal testing instrument at a peeling speed of 5 mm/min.

RESULTS AND DISCUSSION

Surface Hardness

Glow discharge polymerization has an advantage that elements not involved in the monomer used for the glow discharge polymerization can be easily incorporated into the formed polymers if the elements were injected as gas independently of the monomer gas into a discharge state. It is a good example that from the mixture of TMS and nitrogen the polymers containing a large amount of nitrogen are yielded as well as silicon, carbon, and hydrogen.⁵ Therefore, two monomer systems can be considered to obtain siloxanelike polymers by glow discharge polymerization. One is organic silicon compounds having Si—O groups, e.g., Si(OCH₃)₄ (TMOS); and the other is a mixture of silicon compounds having no Si—O groups and oxygen, e.g., the mixture of Si(CH₃)₄ (TMS) and oxygen.

The polymers prepared from TMOS and from the TMS/O₂ mixture by glow discharge polymerization were compared. Table I shows the surface hardness of the polymers prepared from the two monomer systems. The polymers formed were deposited on slide glasses, and their surface hardness was evaluated by the pencil hardness method.⁷ The polymers prepared from the TMS/O₂ mixture, as seen in Table I, are hard, and the surface hardness rises up as the oxygen concentration in the TMS/O₂ mixture increases, while the polymers prepared from TMOS are not as hard as those from the TMS/O₂ mixture.

It can be concluded that the mixture of TMS and oxygen is a favorable system for improvement of surface hardness by glow discharge polymerization.

Successively, the glow discharge polymerization in the system of the TMS/O₂ mixture was applied for improvement of the surface hardness of polymer substrates. The polymer substrates used were high-density polyethylene (PE), poly(methyl methacrylate) (PMMA), polycarbonate (PC), and polytetrafluoroethylene (PTFE), and the surface hardness was evaluated by the pencil hardness method (Table II). Table II shows that the surface hardness of polymer substrates such as PE and PC can be improved by the glow discharge polymerizations in the system of the TMS/O₂ mixture, but there is less improvement in the surface hardness of PMMA and PTFE. The surface hardness of these polymers that were modified by the glow discharge polymerization in the

TABLE I
Surface Hardness of Polymers Prepared from TMS/O₂ and TMOS by Glow Discharge Polymerization

Polymers from (mole ratio)	Surface hardness ^a
TMS/O ₂ 1/0	4H
3/1	5H
1/1	>6H
1/2	>6H
1/3	>6H
TMOS	H

^a Evaluated by the pencil hardness method.

TABLE II
Surface Hardness of Polymer Surfaces Modified in the System of TMS/O₂ Mixture by Glow Discharge Polymerization

Substrate	Surface hardness ^a					
	Untreated	Modified by TMS/O ₂ mixture (mole ratio)				
		1/0	4/1	3/1	1/1	1/2
PE	2B	HB	H		HB	HB
PMMA	4H	4H (5H) ^b		4H (5H)	4H (6H)	4H
PC	2H	3H		3H	3H	3H
PTFE	4B	4B		4B	4B	3B

^a Evaluated by the pencil hardness method.

^b Coated with polymer films that were prepared from the TMS/O₂ mixture by glow discharge polymerization and exposed to Ar-plasma for 5 min.

TMS/O₂ mixture system is fairly low compared with that of the polymer films that were deposited on slide glasses from the same mixture system. This indicates that the surface hardness of the polymer films prepared by glow discharge polymerization may depend on the nature of the substrates on which the polymer films were deposited. Although the surface hardness of the polymer films deposited, indeed, involves effects of rheological properties of the substrates which were coated with the polymer films, a doubt that chemical structures of the formed polymer films may be altered by what substrate was placed in a discharge state to be modified by glow discharge polymerization isn't eliminated because the surface hardness, as presented in parentheses in Table II, rose up when the polymer films deposited on PMMA substrate were exposed again to Ar-plasma for 5 min.

Surface Energy

To distinguish the surface properties of the polymer films that were prepared from the same composition of the TMS/O₂ mixture but were deposited on different substrates, the surface energies of the polymer films deposited on slide glasses and PE substrates were compared (Table III). Table III shows that the surface energies of polymers prepared from the TMS/O₂ mixture by glow discharge polymerization increase as the concentration of oxygen in the mixture increases. It is worth noticing that there is a distinct difference in surface energy

TABLE III
Surface Energies of Polymers Prepared from the TMS/O₂ Mixture by Glow Discharge Polymerization

Composition of the TMS/O ₂ mixture (mole ratio)	Surface energies (dyn/cm)					
	Deposited on glass			Deposited on PE		
	γ_s	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p
1/0	34.4	33.1	1.3	26.8	25.0	1.8
3/1	30.4	28.6	1.8			
2/1				30.4	26.9	3.5
1/1	39.1	33.9	5.2	29.6	22.5	7.1
1/2				61.4	22.4	39.0
1/3	52.6	28.8	23.8			

between the polymer films deposited on slide glasses and on PE substrates. The polymer films deposited on PE substrates possess fairly lower surface energies than those deposited on slide glasses. This indicates that the surface properties of polymer films prepared by glow discharge polymerization are changed by what substrate the formed polymers were deposited on. From this result it can be concluded that there is an alteration in chemical structure between the polymers deposited on slide glasses and on PE substrates.

Although the chemical structures of the polymers formed should be analyzed to discuss influences of the nature of substrates to be deposited on the surface properties of the polymers formed, we can speculate about this difference in the surface properties according to the concept of the CAP (Competitive Ablation and Polymerization) mechanism proposed by Yasuda.⁸ The substrate that were placed in a reaction chamber to be coated with polymer films prepared by glow discharge polymerization are exposed to plasma through the polymerization process and subjected to attack by electron, ions, radicals, etc. being present in the plasma. Accordingly, reactions including degradation and crosslinking reaction will be induced with the evolution of small molecules. Organic substrates such as PE are most susceptible to plasma than inorganic substrates such as glass, and large quantities of small molecules will evolve from the organic substrates to gas phase, i.e., plasma. The gas composition in the reaction chamber during the polymerization, therefore, will be widely scattered from the initial composition of the TMS/O₂ mixture injected into the reaction chamber, and altered polymers will be formed. Meanwhile, from the slide glass a small amount of small molecules will evolve, and the gas composition in the reaction chamber may be retained. This difference in plasma susceptibility between PE and glass seems to reflect on the surface hardness as well as the surface energy.

Adhesion between Plasma Films and Polymer Substrates

The adhesion between polymer films that were prepared from the TMS/O₂ mixture by glow discharge polymerization and the polymer substrates was evaluated by the Scotch tape test and lap-shear strength. The adhesion, as seen in Table IV, is good with the exception of a few combinations. The magnitude of lap-shear strength is about 9–38 kg/cm², which strongly depends on the combination of the polymer substrates and the gas composition in the TMS/O₂

TABLE IV
Adhesion between Polymer Films Prepared from the TMS/O₂ Mixture and Polymer Substrate

Composition of the TMS/O ₂ mixture (mole ratio)	Adhesion							
	PE		PMMA		PC		PTFE	
	Scotch tape test ^a	Lap-shear strength (kg/cm ²)	Scotch tape test	Lap-shear strength (kg/cm ²)	Scotch tape test	Lap-shear strength (kg/cm ²)	Scotch tape test	Lap-shear strength (kg/cm ²)
1/0	+	38.0	+	32.0	±	26.0	-	11.0
4/1	+	35.3						
3/1			+	21.8	+	25.5	±	10.5
1/1	+	33.9	+	18.8	+	28.8	+	11.6
1/2	+		+	18.0	+	23.1	+	8.6

^a +, Not peeled off; ±, partially peeled off; -, completely peeled off.

mixture. The PE substrate shows the largest magnitude of the lap-shear strength, PC and PMMA follow, and PTFE shows the smallest magnitude. The magnitude also decreases slightly as the oxygen concentration in the mixture increases. The failure occurred simultaneously at an interface between the polymer substrate and the polymer films. It is worth noticing that the PE substrate of which the surface hardness could be effectively improved by the glow discharge polymerization of the TMS/O₂ mixture possesses high lap-shear strength enough to be practically used.

From results obtained in this study following aspects are pointed out:

(1) The surface hardness of the polymer substrates can be improved by the glow discharge polymerization of silicon-containing compounds. The TMS/O₂ mixture is more favorable than TMOS for modifying the surface hardness by glow discharge polymerization.

(2) The surface hardness improved by the glow discharge polymerization strongly depends on the nature of the polymer substrates to be modified.

(3) The adhesion between the polymer films prepared from the TMS/O₂ mixture by glow discharge polymerization and the polymer substrates is good.

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