

STUDIES ON LUBRICATING POLYMER SURFACES

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1992

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ABBREVIATIONS

Polymers

EVA	ethylene vinyl-acetate copolymer
Eval	ethylene vinyl-alcohol copolymer (VAECO)
HDPE	high density polyethylene
LDPE	low density polyethylene
PAAm	polyacrylamide
PDMAA	poly(N,N-dimethylacrylamide)
PET	poly(ethylene terephthalate)
PMMA	poly(methyl methacrylate)
PP	polypropylene
PS	polystyrene
PTFE	polytetrafluoroethylene
PVA	poly(vinyl alcohol)
PVC	poly(vinyl chloride)
PU	polyurethane
VAECO	ethylene vinyl-alcohol copolymer (Eval)
6F	tetrafluoroethylene-hexafluoropropylene copolymer

Monomers

AA, AAc	acrylic acid
AAm	acrylamide
AMPS	2-acrylamido-2-methylpropane sulfonic acid
DMAA	N,N-dimethylacrylamide
DMAEA	N,N-dimethylaminoethyl acrylate
DMAEMA	N,N-dimethylaminoethyl methacrylate
DMApAA	N,N-dimethylpropyl acrylamide
NaSS	styrene sulfonate
VA	vinyl acetate

Others

ATR	attenuated total reflection
DPPH	1,1-diphenyl-2-picrylhydrazyl
LC	lumichrome, 6,7-dimethyl-alloxazine
LCST	lower critical solution temperature
RF	riboflavin, 6,7-dimethyl-1-(D-1'-ribityl)-isoalloxazine
	radio frequency
SEM	scanning electron microscope
SIMS	secondary ion mass spectroscopy
XPS	X-ray photoelectron spectroscopy

GENERAL INTRODUCTION

Most of the surfaces of polymers used in industry are not hydrophilic but hydrophobic. Therefore, it is difficult to directly bond these nonpolar polymer surfaces with other substances like adhesives, printing inks, and paints which generally consist of polar compounds. In addition, the polymer surfaces are not extremely so hydrophobic as to completely reject adhesion of other objectives. It should be also pointed out that a transparent polymer surface becomes translucent when exposed to high humidity at temperatures below the dew point because of deposit of minute water droplets on the surface. An exception is the regenerated cellulose film with lots of polar groups on and in the surface region. Static electrification is also closely related to the surface properties of polymer. Therefore, surface modifications of polymer have been an important technology in polymer applications from the advent of polymer industries.

The background and concept for surface modifications of polymeric materials are completely different from those of metals. In the case of coating on metallic materials, surface treatment is mostly performed to protect the poor bulk properties (e.g. iron from staining or erosion). In the case of polymers, their bulk properties should be excellent, regardless of surface modification. The purpose of surface modification for polymers is to impart new properties which the bulk polymer does not possess. The properties characteristic to polymer surfaces include wettability, adhesiveness, printability, electrostatic properties such as triboelectrification and electroconductibility, anti-fogging, anti-fouling, grazing, surface hardness, surface roughness, biocompatibility, and lubricity and so forth. Among these properties, wettability, printability, and adhesiveness can be generally improved by making the surface of polymers hydrophilic. The modification of polymer surface can be achieved with physical modification methods without using any wet chemical reagents. For this purpose, various high energy sources are employed such as treatment with ion beam, plasma [1-10], oxidization with ozone [11,12], and irradiation with ionizing [13-18] and nonionizing radiations[19-25].

In Part I of this thesis, characteristics of polymer surfaces and graft polymerization with

the use of UV light were described. Although a variety of analytical methods are currently available for characterizing polymer surfaces, for instance, Fourier-transform infrared spectroscopy (FT-IR) coupled with attenuated total reflection (ATR), XPS, Auger electron spectroscopy, and secondary ion mass spectroscopy (SIMS). However, contact angle measurement is still very common because of ease of use and relatively low cost. In addition, the contact angles give information on the outermost layer of surface. Chapter I is concerned with methods of measuring the contact angle in three different manners, that is, two types of sessile drop method and the Wilhelmy plate technique.

It is well known that UV irradiation also results in build-up of hydroperoxides for many polymers[26-31]. In Chapter II, surface analysis of UV-irradiated films will be undertaken with the combination of X-ray photoelectron spectroscopy (XPS) analysis and water contact angle measurement. Quantitative analysis of formed peroxides groups is also performed with a DPPH method.

Surface properties of polymers are often as important as their bulk properties. Therefore, there have been reported a variety of surface modification methods. The methods investigated for the surface grafting involve either immobilization of existing polymer chains onto a polymer surface by coupling reactions or graft polymerization of monomers. The use of UV irradiation seems to be an excellent method because of simplicity and cleanness of its treatment. As demonstrated in Chapter I, UV irradiation results in build-up of hydroperoxides for many polymers, regardless of the presence of photosensitizers. These peroxides may function as an efficient initiator for surface grafting, similar to irradiation with high energy radiation and plasma treatment. Chapter III will describe the results of graft polymerization of acrylamide (AAm) onto films such as nylon 6, polypropylene (PP), and ethylene-vinyl acetate copolymer (EVA).

The generation of electrostatic charges on polymers has been mostly a nuisance in many fields associated with polymer and textile technologies. In addition to discomfort from static cling or static discharge, it often causes serious damage in semiconductor manufacture and sometimes to human life through fire or explosion. Many efforts have been made to minimize

the electrostatic charging, for instance, by rendering the polymer surfaces hydrophilic or electroconductive. The methods employed include surfactant mixing and metal fiber coweaving. Surface modifications of polymeric materials have been also studied in an attempt to reduce the generation of electrostatic charges[32-34]. In Chapter IV, polystyrene and poly(ethylene terephthalate)(PET) films were irradiated with UV radiation and further surface-grafted with hydrophilic monomers. The electrostatic properties of these UV-irradiated and surface-grafted polymers were studied by charging through mechanical rubbing or exposure to high electric fields.

It was found that a polymer surface modified by graft polymerization of water-soluble monomers shows substantial adhesion to another surface when brought into contact in the presence of water and subsequently dried. Chapter V was undertaken in an attempt to investigate the adhesion of grafted surface to other substrates with different wettabilities without applying any adhesives. For this purpose, the surface of a PET film was graft-polymerized with water-soluble, nonionic and ionic monomers by a photoirradiation technique, the adhesion force was measured between two polymer films after being contacted with water under a load.

Surface modifications of polymer materials have been the objective of a large number of investigations, but little attention has been paid to make a polymer surface frictionless or slippery. Such a frictionless surface is nonetheless important, especially in the field of marine and biomedical technologies. Lubricating polymer surfaces were overviewed in Part II, dealing with the principle, technology, and applications. A coefficient of friction (μ value) is commonly used for evaluation of the lubrication of surfaces, but often difficult to determine, especially for elastic and adhesive polymers because of their complicated hysteresis occurring in a cycle of deformation and recovery during the frictional motion, which is probably associated with adhesion force and displacement force. The aim of Chapter VI is to modify polymer surfaces by graft polymerization and determine their μ value in a hydrated state. Polypropylene(PP), nylon 6, and ethylene-vinyl acetate copolymers(EVA) were employed as substrate polymers, and acrylamide(AAm) and N,N-dimethyl acrylamide(DMAA) were used as nonionic water-soluble

monomers.

Polymeric materials with a slippery or low-frictional surface are valuable in biomedical technologies. When biomaterials are to be used for catheterization in urinary, tracheal, and cardiovascular tract, or for endoscopy, their dried surface should be provided with good handling characteristics and is further desired to become slippery upon contact with aqueous body liquid to prevent mucous membranes from their mechanical injury and lessen pain of patients[35]. Currently, smooth catheterization is achieved by applying lubricants or jelly-like materials or coating a hydrogel onto the catheter surface. Lidocaine jelly is commonly used because of its additional local anaesthetic effect. However, these agents applied on catheters are not effective after a long period of dwelling time, due to their elution into the adjacent body liquid. The hydrogel coating does not give a highly slippery surface for long times, compared with the surface grafting of water-soluble polymers. Chapter VII describes the methods to prepare such catheter materials as possessing low frictional surface. EVA and plasticized poly(vinyl chloride)(PVC) were chosen as the substrates and DMAA as the monomer.

The total frictional force between two polymeric surfaces is somewhat complicated due to surface roughness, mechanical integrity of boundary layer, viscoelastic energy dissipation, van der Waals interaction, and electrostatic and polar interactions between the surface molecules. In the course of studies on the lubricious surfaces modified by graft polymerization, it was found that the surface structure observed by scanning electron microscopy(SEM) depended on the process of sample preparation for the SEM observation. For instance, a peculiar textured structure was observed when the hydrated grafted surface was subjected to freeze-drying for SEM sample preparation. Chapter VIII represents the result, focusing on the surface morphology observed by SEM.

It would be interesting if the lubricating surface described so far can be applied, for instance, to the wall of a pipe transporting fluid or to the surface of a boat or an aircraft to increase the volume flow of fluid or the craft speed. The drag reduction has been accounted for in terms of decreasing turbulence, wall effect (not related to the surface nature of pipe, but to the

shear thinning wall layer), adsorption effect, stretching of polymer molecules in flow, and so forth [36]. Walsh intensively studied the drag reduction of turbulent boundary layer using riblets[37-39] and concluded that the maximum drag reduction by the V-groove riblet was dependent on the height and spacing of the riblets in law-of-the-wall variables, regardless of the free-stream Reynolds' number or upstream boundary-layer history. The V-groove riblet having the optimal structure in height and spacing exhibited 7 to 8 % drag reduction. Chapter IX examined the effect of surface lubricity on the drag reduction using a surface-grafted high density polyethylene(HDPE) and polyurethane tube.

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PART I

BASIC STUDIES ON LUBRICATING SURFACES

PROBLEMS ASSOCIATED WITH CONTACT ANGLE MEASUREMENTS

INTRODUCTION

A variety of analytical methods are currently available for characterizing polymer surfaces in addition to contact angle measurement. They include Fourier-transform infrared spectroscopy (FT-IR) coupled with attenuated total reflection(ATR), X-ray photoelectron spectroscopy(XPS), Auger electron spectroscopy, and secondary ion mass spectroscopy(SIMS). However, contact angle measurement is still very common because of ease of use and relatively low cost. In addition, the contact angle gives information on the outermost layer of surface within 1 nm depth[1]. This is in contrast with XPS which provides information on the elemental ratios and functional groups of polymer surfaces within 5 nm. Thus, using contact angle information such as hydrophilicity-hydrophobicity balance, overturn of functional groups at the outermost surface, and microscopic roughness can be obtained.

There are different methods for measuring the contact angle[2-4], including the sessile drop and the adhering gas bubble method, the Wilhelmy-gravitational method, the capillary rise at a vertical plate, the tilting plate method, the reflection method, etc. Each of these methods has its merits and limitations. The aim of this Chapter is to compare the contact angles of water on various polymeric materials determined in three different manners, that is, two types of sessile drop method and the Wilhelmy plate technique.

The determination of contact angles against a sessile water droplet is carried out using a conventional telescope and laser reflection. The contact angle determination with the Wilhelmy methods is performed automatically by utilizing a commercially available apparatus.

EXPERIMENTAL

Materials

The following films were employed for the contact angle measurement; regenerated cellulose, PVA, EVAL of 77% ethylene unit, nylon 6, PET, PMMA, a segmented PU, PS, HDPE, PP, and a tetrafluoroethylene-hexafluoropropylene copolymer of 33 mol% tetrafluoroethylene (6F). The PMMA, PS, and PU films were prepared by casting the respective polymer solution on a clean glass plate. All other polymer films were of commercial grade with the thickness ranging from 20 to 100 μ m. They were purified by Soxhlet extraction for 24 h with the appropriate solvent, dried under a reduced pressure, placed between two leaves of filter paper and stored in a desiccator kept at 25°C and 60 %RH.

Contact Angle Measurements

All measurements were performed in a clean batch maintained at constant temperature(25° C) and humidity(60 %RH) using doubly distilled water. The following is a brief description of the methods used.

a. Sessile drop method with a telescope

The stationary contact angle against a water droplet ranging from 0.5 to 1.0 mm in diameter was measured using a telescopic goniometer(M2010-6GII type, Elma Inc., Tokyo, Japan). The telescope having magnification of 30 power was equipped with a protractor graduated by 1°.

b. Sessile drop method with laser beam

The laser-beam contact angle measurement was carried out with the method established in 1982 by Israel et al.[5] and Kishi[6]. The instrument consists of optical components including a laser source, a filter, a sample stage, and a screen on an optical bench, as shown in Figure 1. The laser beam reflected from the solid-liquid-air interface is projected onto the screen normal to the incident beam at an angle α which is related to the contact angle θ by Eq.(1).

$$\theta = 90^\circ - \alpha \quad (1)$$

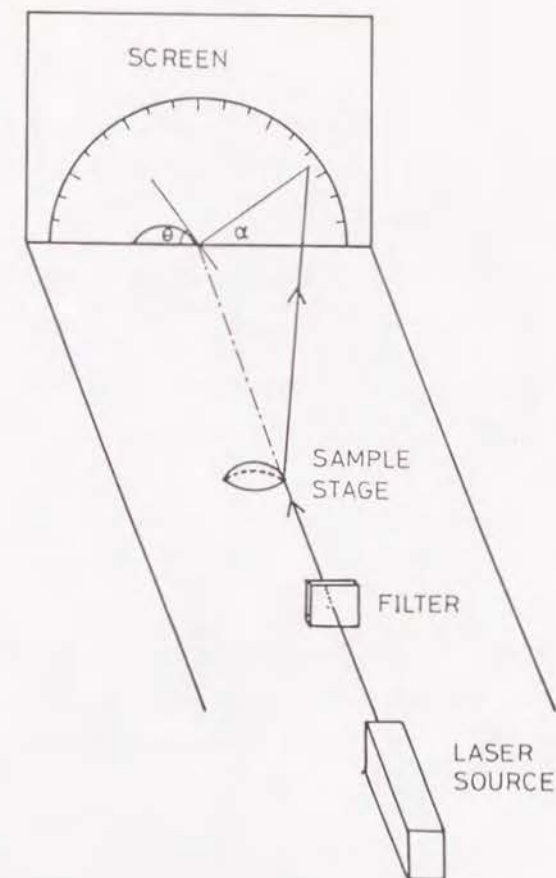


Fig. 1. Schematic representation of contact angle measurement by laser beam. The size of the liquid droplet and its shadow on the screen is depicted in an exaggerated manner.

As the projected beam on the screen is clear and large, one can easily determine the contact angle within $\pm 0.2^\circ$ with the naked eye using a protractor drawn on the screen in relatively large scale graduated by 0.2° . The beam employed in the present work is a He-Ne laser of 632.8 nm wave length and has a less than 1 mW power.

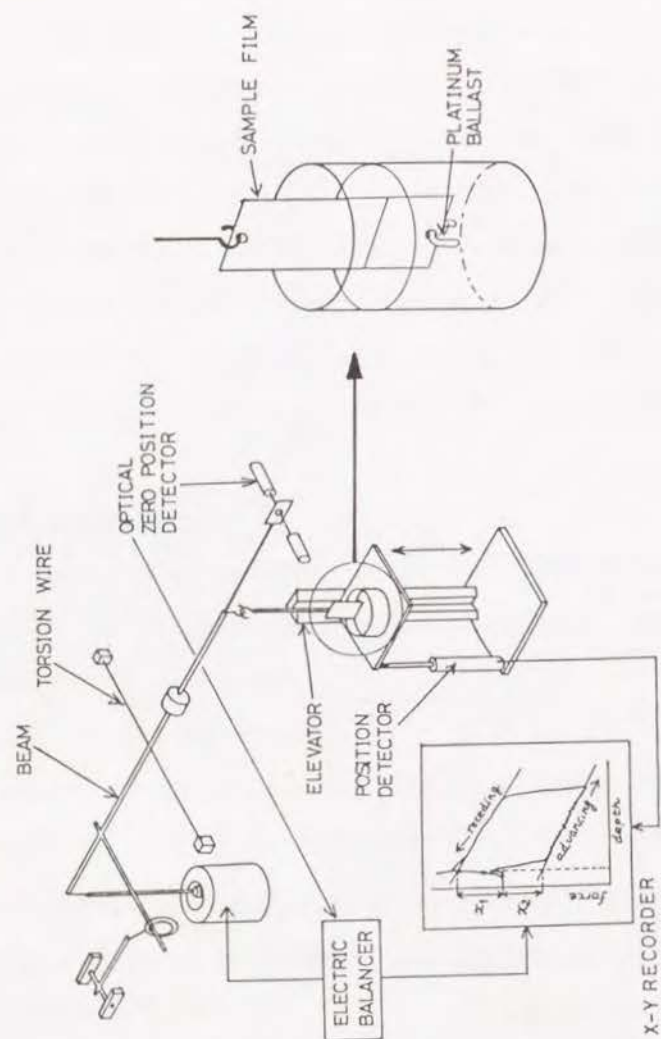


Fig.2. Schematic representation of the apparatus to determine advancing and receding contact angles by the Wilhelmy plate technique.

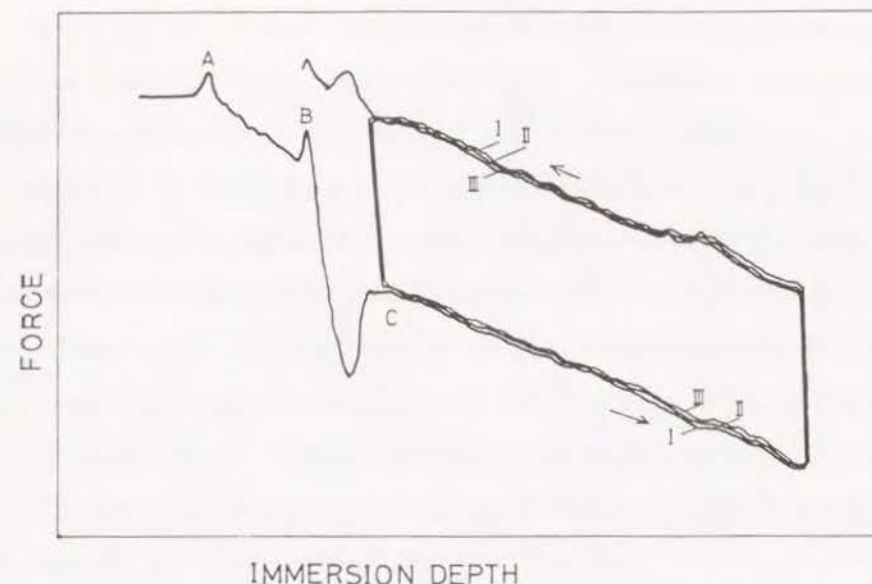


Fig.3. Hysteresis loop observed for a high density polyethylene film by the Wilhelmy plate technique at an immersion rate of 10 mm/min. (see the text for explanation of A-C and I-III)

c. Wilhelmy plate method

An apparatus (Automated System for Dynamic Contact Angle Measurement, ST-1S type) manufactured by Simadzu Inc., Kyoto, Japan, was used in the present work. The structure of this apparatus is schematically depicted in Figure 2. The principle of determining the contact angle by this method is similar to that described by Andrade et al.[7-11]. Most of the polymeric materials have a density less than 1.0 g/cm^3 , often making it difficult to immerse the polymer films deeply into water because of film floating on the water surface. Andrade et al. used a glass plate coated with the polymer. Instead of using such a heavy glass plate, the polymer film whose contact angle was to be measured was immersed directly in water providing a load at the film bottom, as illustrated in Figure 2. An example of the results obtained for the HDPE film against water is shown in Figure 3. The sample film with a platinum(Pt) load is allowed to be immersed at a contact speed into purified water. When

the Pt load and subsequently the HDPE film touch the water, the surface meniscus is formed in both cases (A and B in Figure 3). Until the Pt load is completely immersed into water, the curve of the chart is meaningless (from B to C in Figure 3). As the sample film gets into water, the surface tension of water on the film remains constant, but the film buoyancy linearly increases, resulting in a constant slope on the X-Y recorder. The extrapolation of the curve to B at the y ax gives the advancing contact angle of the surface of the HDPE film. After scanning up to some immersion distance, the movement of the water container is reversed to lower the surface of water and the force exerted by the film is measured by the electric balance to determine the receding contact angle. Unless the Pt load is used, the advancing (θ_a) and receding (θ_r) contact angles would be calculated according to Eqs.(2) and (3).

$$F_a = \gamma L \cos \theta_a \quad (2)$$

$$F_r = \gamma L \cos \theta_r \quad (3)$$

where F_a and F_r are the force at zero depth of immersion of the sample film at advancing and receding scanning, respectively. γ is the surface tension of the tested liquid and L is the peripheral of the sample film. When the film is immersed into the liquid with the Pt load, the factor due to buoyancy of the Pt load should be added. Thus, one can obtain

$$F_a = \gamma L \cos \theta_a - Mg/d \quad (4)$$

$$F_r = \gamma L \cos \theta_r - Mg/d \quad (5)$$

where g , M , and d are gravitational acceleration, the mass, and the density of Pt load, respectively.

RESULTS AND DISCUSSION

Telescopic Contact Angle

The contact angles of water on the polymer surfaces often vary depending on the time after deposition of the water droplet and on the size of the water droplet. The time dependence of the contact angle is shown in Figure 4 for 6F, EVAL, and cellulose. As is clearly seen, the contact angle of these films slightly decreases with time, and the rate of this decrease is higher for the film having a more hydrophilic surface. The decrease of the contact angles with time may be explained in terms of swelling of the polymer matrix with water, reorientation of segments existing near the surface region due to contacting with water[12], and change of the size of droplet, due to water evaporation with time. To study the effect of the droplet size, the contact angle of EVAL film was determined with different sized water droplets as shown in Figure 5. These results were obtained when the measurement was performed one minute after placing the droplet on the film surface. Although somewhat lower contact angles are observed here with smaller droplets, the changes are in the range of the experimental error (3 to 5) which is primarily due to the optical obscurity in the view field of telescope. Thus, it is likely that the water droplet size has little effect on the contact angle, compared with the reduction of contact angle with time. It is recommended to extrapolate the observed sessile contact angle to time zero, especially for hydrophilic surfaces.

Laser Beam Contact Angle

The effects of the droplet size and the time dependence of contact angles determined by the laser beam were similar to those obtained by the telescopic sessile drop method. Israel et al.[5] also studied the effect of droplet size for the stationary contact angles of PMMA and glass and found that the contact angle decreased with the decreasing droplet size. However, the difference in the contact angle was as small as 2.6° when the droplet size was enlarged from 0.2 to $10\mu\text{l}$. It was found that the contact angle deviation from the average was as small as $\pm 0.5^\circ$ for ten readings of EVAL and cellulose.

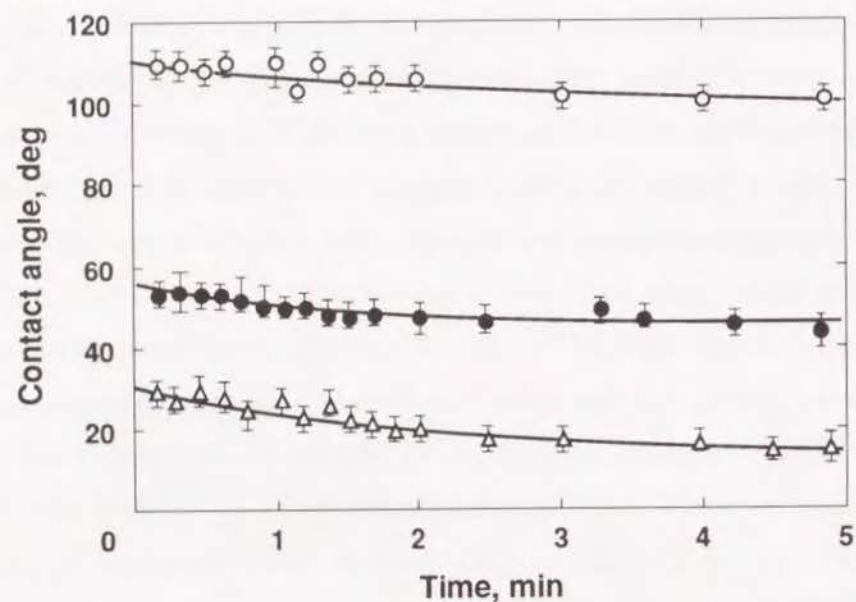


Fig. 4. Time dependence of water contact angle measured by a telescopic sessile drop method.

○ ; tetrafluoroethylene-hexafluoropropylene copolymer, ● ; ethylene-vinyl alcohol copolymer, Δ ; cellulose.

A typical photograph demonstrating the reflected laser beam on the screen is shown in Figure 6 for the measurement of cellulose film. In this case, α is 65° and hence θ is 25° . As the laser beam projected on the protector scale is sufficiently large and clear, the error associated with reading the angle is less than $\pm 0.1^\circ$. The observed experimental error deviation of $\pm 0.5^\circ$ is probably due to the heterogeneity of the film surface. Thus, the laser beam method seems to be more accurate than the telescopic one to measure the sessile drop contact angles. However, contact angles greater than 90° cannot be determined with the laser method, because the reflected laser beam yields only the angle α on the protractor. The contact angle θ is then calculated from α according to Eq.(1). Thus, the contact angle of 6F film by the laser beam goniometry could not be determined.

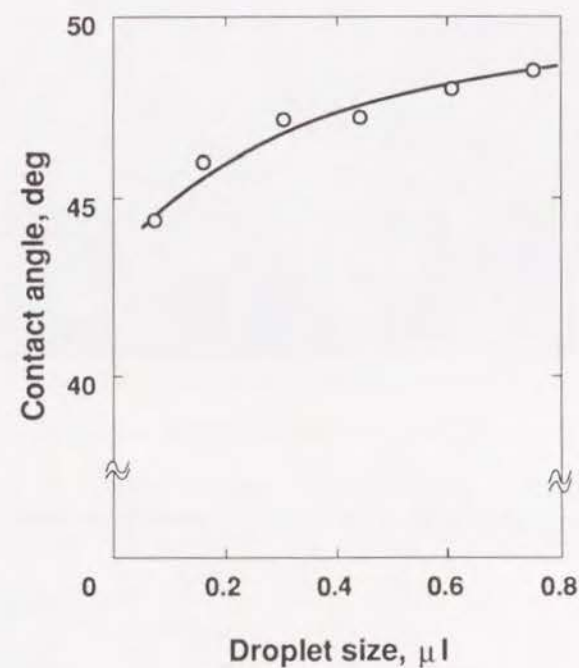


Fig. 5. Effect of the droplet size on the contact angle of an ethylene-vinyl alcohol copolymer film determined by the telescopic contact angle method.



Fig. 6. A typical projection of a laser beam from a drop of water on a cellulose film.

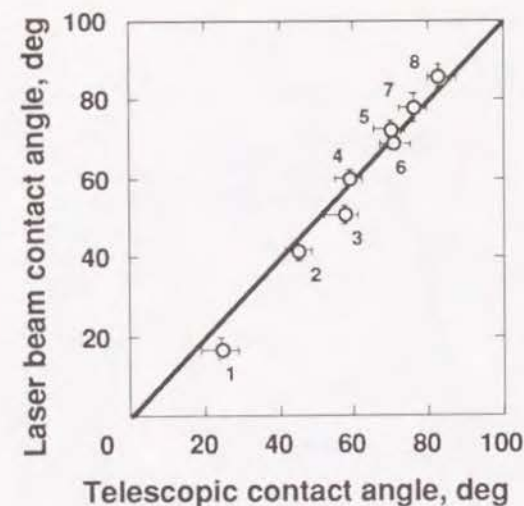


Fig. 7. Relation between the laser beam and the telescopic contact angles.
1. cellulose, 2. poly(vinyl alcohol), 3. ethylene-vinyl alcohol copolymer, 4. nylon 6, 5. poly(ethylene terephthalate), 6. poly(methyl methacrylate), 7. polyurethane, 8. polystyrene.

A comparison of the contact angles obtained by the telescopic and the laser beam goniometry for various polymer films is shown in Figure 7. The contact angle measurement was done one minute after placing a droplet of 0.45 μl on the surface. The mean values of ten readings by both the methods are plotted in Figure 7, together with the error bar which demonstrates a maximum and a minimum of each reading. It is clearly observed that the two methods yield identical results, but the experimental error of the laser beam method is smaller than the telescopic method.

Wilhelmy Contact Angle

The hysteresis loops for the films having hydrophobic surface were determined by the Wilhelmy method. The results obtained for 6F and PP are shown in Figure 8. The result obtained for HDPE was already given in Figure 3. These data indicate no significant

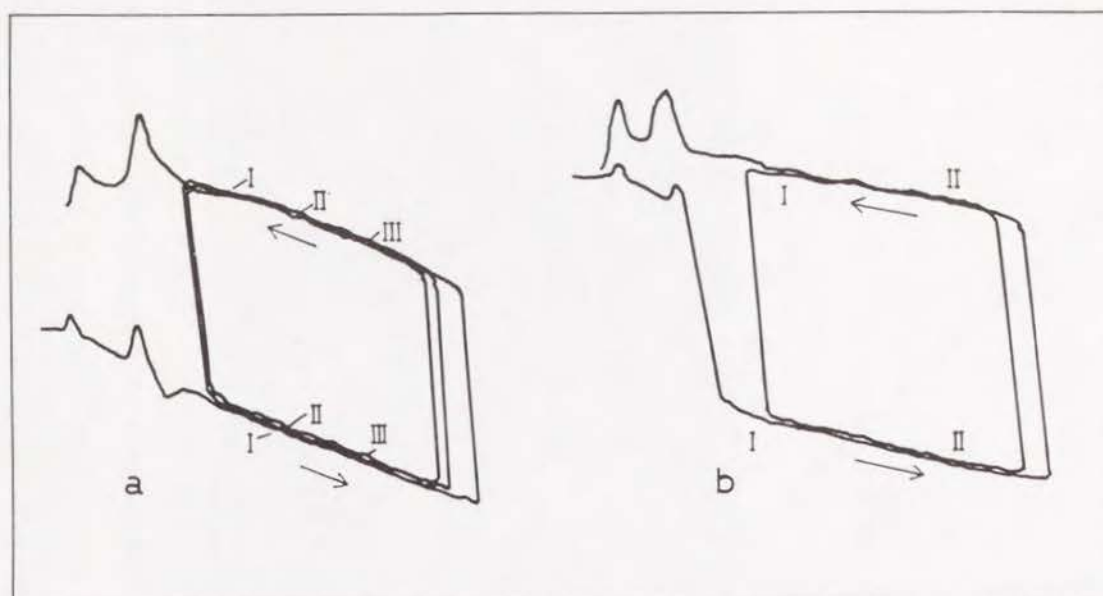


Fig.8. Wilhelmy hysteresis loops for hydrophobic films of polypropylene (a) and tetrafluoroethylene-hexafluoropropylene copolymer (b) at an immersion rate of 10 mm/min.

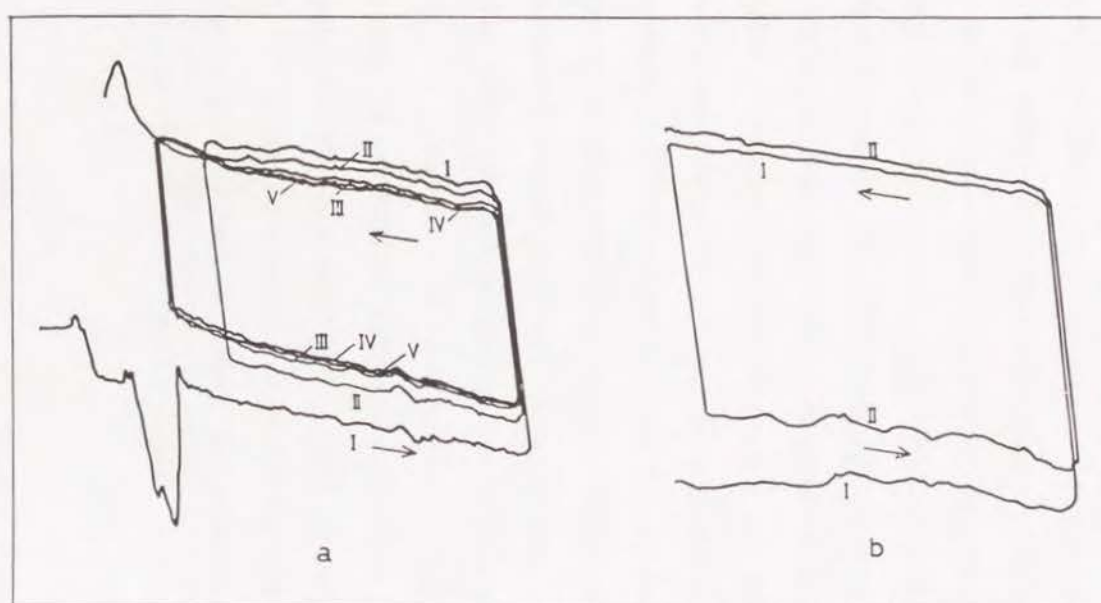


Fig.9. Wilhelmy hysteresis loops for moderately hydrophobic films of polyurethane (a) and ethylene-vinyl alcohol copolymer (b) at an immersion rate of 10 mm/min.

difference between the first, the second, and the third loop. Thus, for these hydrophobic surfaces, θ_a and θ_r of the films in contact with water is independent of time. This conclusion is in good agreement with the observations by the sessile drop methods. The less hydrophobic PU and EVAL films give rise to hysteresis loop with a different dependence on the cycle of immersion (Figure 9). Even more drastic differences are observed for the hydrophilic cellulose and PVA films where the advancing slope gave a profile quite different between the first and the second immersion, as shown in Figure 10. In measuring the contact angle of very hydrophilic surfaces with the Wilhelmy method, the surfaces of specimen will be completely hydrated once it is allowed to be fully immersed in water. Therefore, the dependence of the contact angle on the time of contacting with water is hard to follow in the case of Wilhelmy method, even though the measurement of the hysteresis loop could be achieved in a very short period of time because of irreversible, time-dependent hydration of the hydrophilic films. According to our observation, the up and down speed of the liquid container had little influence on the hysteresis loop for every sample studied in the present work, so far as the speed was changed from 1 to 10 mm/min.

There can be many factors that affect the difference and thus the contact angle hysteresis between θ_a and θ_r . These include surface roughness, adsorption, water swelling, and rearrangement of segments existing on the polymer surface [12-17]. However, although the reason for the hysteresis can be clarified, it is still not easy to predict the stationary contact angle from θ_a and θ_r . Thus, we simply assume that the mean contact angle θ_m is given by the Eq.(6). [18]

$$\cos \theta_m = 1/2 (\cos \theta_a + \cos \theta_r) \quad (6)$$

The values θ_m calculated from θ_a and θ_r of the second hysteresis are plotted against the stationary contact angles as determined by the laser beam method in Figure 11. It is clearly seen from Figure 11 that the agreement between the two methods is satisfactory.

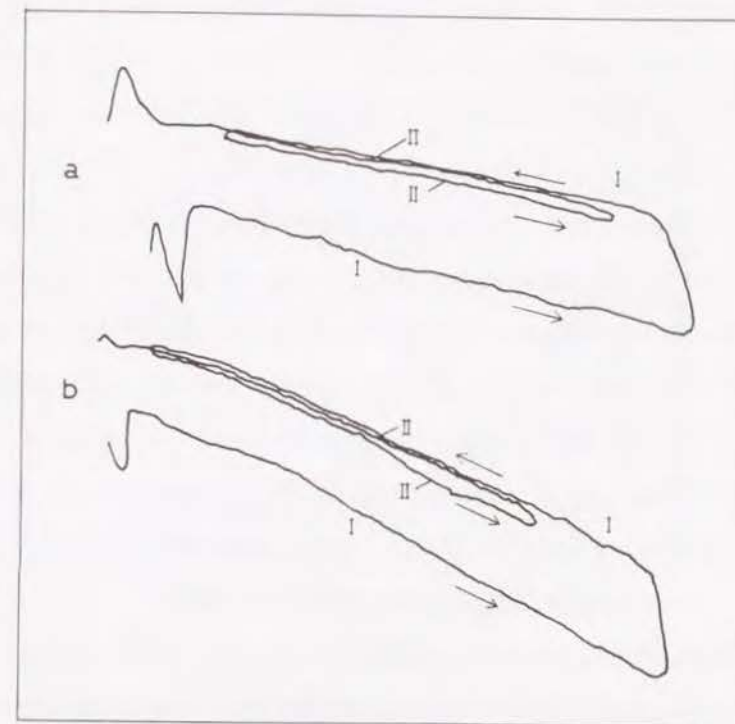


Fig. 10. Wilhelmy hysteresis loops for highly hydrophilic films of cellulose (a) and poly(vinyl alcohol) (b) at an immersion rate of 10 mm/min.

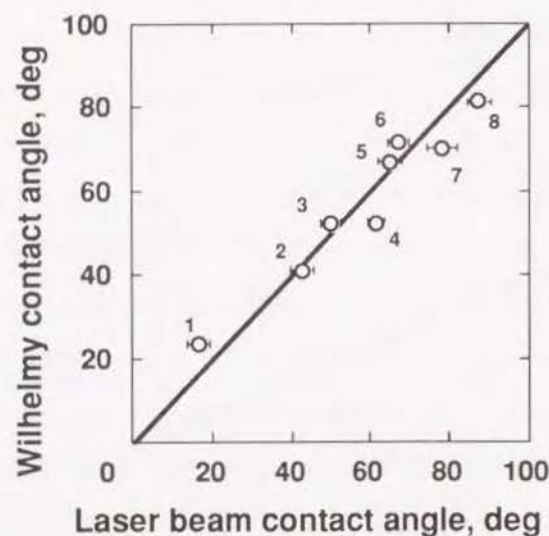


Fig. 11. Relation between the stationary contact angle determined with the laser beam goniometry and the mean contact angle calculated from the advancing and receding contact angles measured with the Wilhelmy plate technique.
1. cellulose, 2. poly(vinyl alcohol), 3. ethylene-vinyl alcohol copolymer, 4. nylon 6, 5. poly(ethylene terephthalate), 6. poly(methyl methacrylate), 7. polyurethane, 8. polystyrene.

CONCLUSION

Three methods were employed in this study for the contact angle measurement. They involve the commonly used telescopic sessile drop method, the newly developed laser beam goniometry, and the automatically driven Wilhelmy plate technique. It was observed that the telescopic sessile drop method and the laser beam goniometry method gave identical contact angles on a wide variety of surfaces ranging from hydrophobic to hydrophilic in nature. The experimental error associated with the laser beam goniometry was smaller than that obtained from the telescopic sessile drop method. The mean contact angles derived from the Wilhelmy plate method were also in good agreement with the contact angles derived from the other two methods. However, this Wilhelmy method is the only one that allows easy measurement of the contact angle hysteresis. Since the contact angles obtained from all these methods are in good agreement, the choice of method could be determined by other factors such as the time required for measurement, the error range, and the nature of the observed contact angle (Table I).

The telescopic sessile drop method has been most widely applied for a long time. It is possible to determine the dynamic contact angles (θ_a and θ_r) by the use of inverted bubble technique. However, the operator must be trained skillfully enough to correctly read the telescopic view. Otherwise, the reading error of $\pm 5^\circ$ is common.

The laser beam goniometry is better than the telescopic method, as is simpler and clearer. It should also be stressed that the apparatus for the laser source is generally less expensive than the telescopic goniometer. In addition, a water droplet as small as $0.05\mu\text{l}$ can be used for the laser beam method. Therefore, it will be possible to determine the contact angle on a small surface of specimen such as monofilament fiber. The major drawback of the laser beam method is the difficulty in determining contact angles around 90° and larger, as well as applying it to the inverted bubble method.

The Wilhelmy plate technique is the most suitable to study the dynamic hysteresis of polymer surface. It provides information on surface transitions on a short time scale, roughness, surface heterogeneity, and adsorption. The disadvantage of this method over

others is that the apparatus is complicated, relatively expensive, and requires a long time to get to data for one sample. However, the results obtained by this method are very accurate and reproducible. Moreover, this method does not involve any operator's subjective errors and makes possible to fabricate an automated instrument coupled with a computer.

Table I Comparison of the methods for determining contact angles.

	Telescopic	Laser beam	Wilhelmy
Measurement time, min	<2	<2	10
Error range, deg	±3 to ±5	±0.5	depends on mechanical precision
Hysteresis determination	possible	possible only on turnable stage	very easy
Features	most widely available	hard to apply to larger than 90° and bubble method	easy to get dynamic hysteresis

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Chapter II

UV IRRADIATION OF POLYMER SURFACE

INTRODUCTION

The use of UV irradiation appears to be an excellent method for surface modification of polymeric materials because of its simplicity and the cleanliness of the treatment. Tazuke et al.[1] summarized the characteristics of the photochemical method for surface grafting of polymers as follows; 1) Photochemically produced triplet states of carbonyl compounds can abstract hydrogen atoms from almost all polymers so that graft polymerization may be initiated. 2) High concentration of active species can be produced locally at the interface between the substrate polymer and the monomer solution containing a sensitizer when photoirradiation is applied through the substrate polymer film. 3) In addition to the simplicity of the procedure, the cost of energy source is lower for UV radiation than for ionizing radiation.

Many methods are known to chemically modify polymer surfaces through graft polymerization with the use of UV light. They may be carried out either under a wet condition (graft polymerization of monomer in solution) or under a dried condition (vapor phase graft polymerization). Earlier studies of Oster et al. [2,3] revealed that UV light exposure led successfully to crosslinking of polyisobutylene, PP, and PMMA in the presence of sensitizers, and to photo-induced graft polymerization of monomers onto polymers blended with photosensitizers. The objective of their work was to find substitutes for silver bromide currently still used in photographic technologies. Charlesby et al.[4] quantitatively analyzed the cross-linking results of PE by UV radiation, reported by Oster et al. A more detailed study was undertaken by Takakura et al.[5], who showed that a PVA film could be crosslinked by UV irradiation in the presence of sodium benzoate as a sensitizer, always accompanied by photolysis

of sodium benzoate used as a sensitizer. The gel content increased with the irradiation time and approached a limiting value, depending on the initial sensitizer concentration.

It is also well known that UV irradiation results in a build-up of hydroperoxides for many polymers, regardless of the presence of photosensitizers, followed by polymer degradation[6-8]. The use of UV light seems to be more simple in treatment and instrumentation for physical modification method without using wet chemical reactions. In order to establish a simplified clear method for surface modification of polymeric materials with the use of UV light, UV irradiation technique is utilized throughout this thesis. The UV light source employed commonly are medium-pressure or high-pressure mercury lamp which emits UV of wavelength about 200 - 300 nm. The present study chosen a high-pressure mercury lamp which does not produce any significant amount of ozone which may oxidize polymers.

The characterization of UV-irradiated films is undertaken in this chapter with the combination of XPS analysis and water contact angle measurement. Quantitative analysis of peroxides groups formed upon UV irradiation is also performed chemically utilizing a DPPH method.

EXPERIMENTAL

Films

Films of nylon 6, PP, HDPE, PET, PS, PVC, PMMA, EVA (VA content = 14, 19, and 28 mol%), and VAECO (ethylene content = 33 mol%) were of commercial grade, mostly having a thickness around 20 μm . Purification of these films were carried out by Soxhlet extraction with acetone or methanol for 24 h.

UV Irradiation

UV irradiation of films was performed with a high-pressure mercury lamp (75 W,

Toshiba SHL-100UV type, $\lambda > 254$ nm) without any cutoff filter. Dried films were irradiated in air at ambient temperature by placing them 7 cm away from the center of the light source.

Surface Analysis

XPS(ESCA) spectra of films were recorded with a Shimadzu ESCA-750 spectrometer using Mg-K α excitation radiation. UV-irradiated films were subjected to analysis immediately after UV exposure within 30 min.

The amount of peroxides generated on the film was determined by the 1,1-diphenyl-2-picrylhydrazyl (DPPH) method. This method was intensively studied by Carley and Kitze with the help of tertiary diamine catalyst[9]. In the present work, thermal decomposition of peroxides and the subsequent reaction with DPPH was adopted instead of using the catalyst. Briefly, the UV-irradiated films were placed in deaerated benzene containing 1.18×10^{-4} M of DPPH. After heating the benzene mixture at 70°C for 24 h, the optical density was measured at 520 nm (OD_{520}) on the benzene solution. The amount of peroxides per liter of DPPH solution was calculated from $\text{OD}_{520} / 2 \times \epsilon_{520}$, where OD_{520} is a difference of OD_{520} between the starting and the irradiated film. The molar extinction coefficient, ϵ_{520} of DPPH is $1.18 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$.

The surface hydrophilicity of the films was evaluated by measuring their contact angle against water at 25°C and 65 %RH with a sessile drop method using a 3 μL water droplet in a telescopic goniometer (M2010A-6II type, Elma Inc., Tokyo). The telescope with a magnification power of 30 X was equipped with a protractor of 1° graduation. At least ten measurements on different surface locations were averaged. The scattering of reading was $\pm 5^\circ$.

RESULTS AND DISCUSSION

Nylon 6 and PP Films

XPS spectra of the UV-irradiated nylon 6 films are shown in Figure 1, together with the unirradiated film. As is seen, N_{1s} and C_{1s} spectra do not exhibit a significant change upon UV irradiation, whereas O_{1s} spectra seem to have a new shoulder appearing at a high binding energy upon irradiation. This finding implies that oxygen atoms other than those in amide bond must be introduced on the surface of nylon 6 films. In Figure 2, differential O_{1s} core level spectra are shown, multiplying their intensity by a factor of 10. It is clearly seen that UV irradiation produces a new spectrum at a binding energy of 1.5 eV higher than that of the starting film. This new spectrum probably corresponds to oxygen of peroxides formed upon UV irradiation.

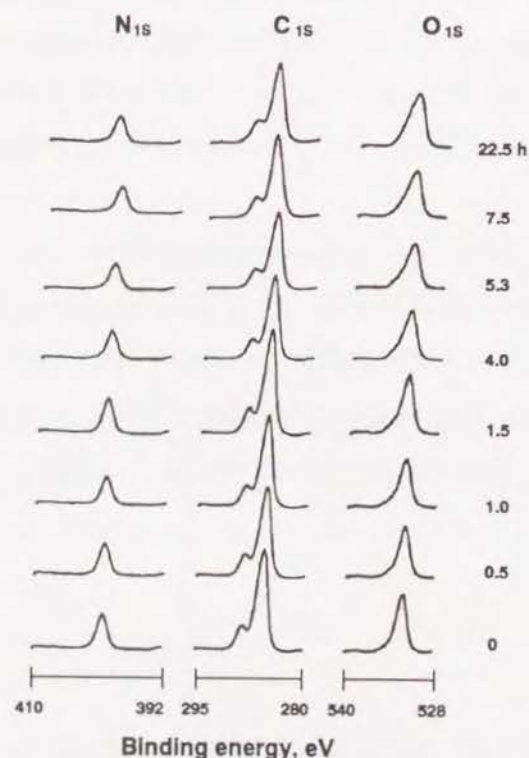


Fig. 1. N_{1s} , C_{1s} , and O_{1s} XPS spectra of nylon 6 film untreated and exposed to UV radiation for different times.

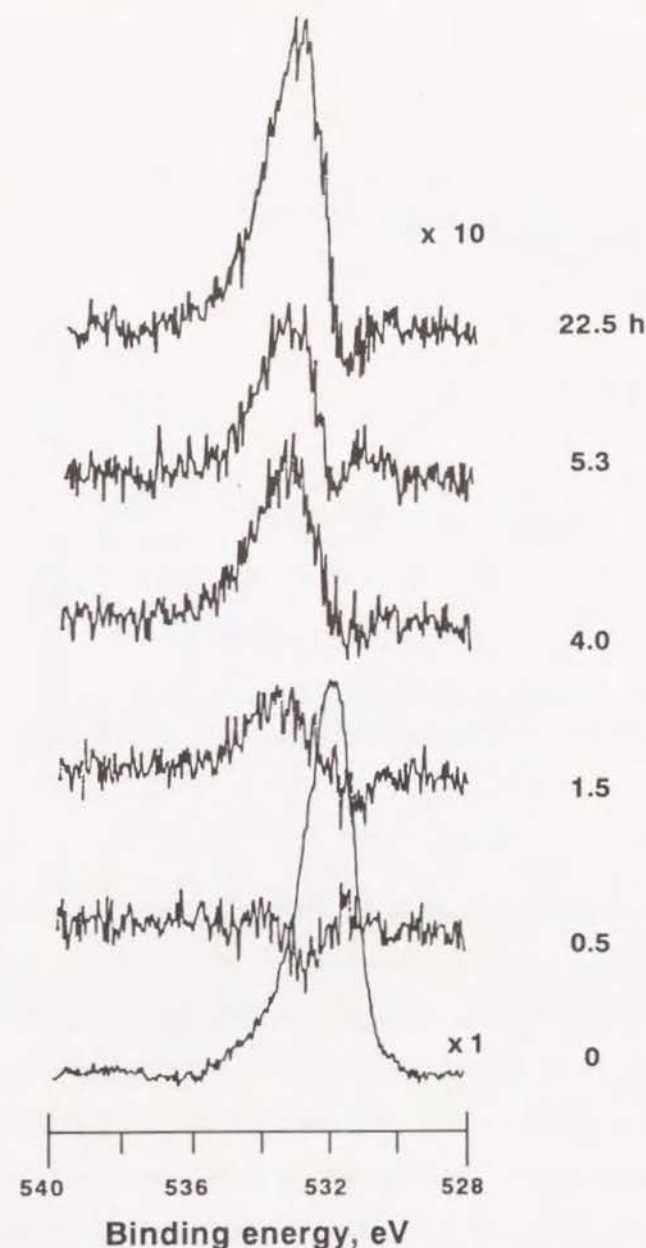


Fig. 2. Differential O_{1s} core level spectra for nylon 6 film exposed to UV radiation for different times.

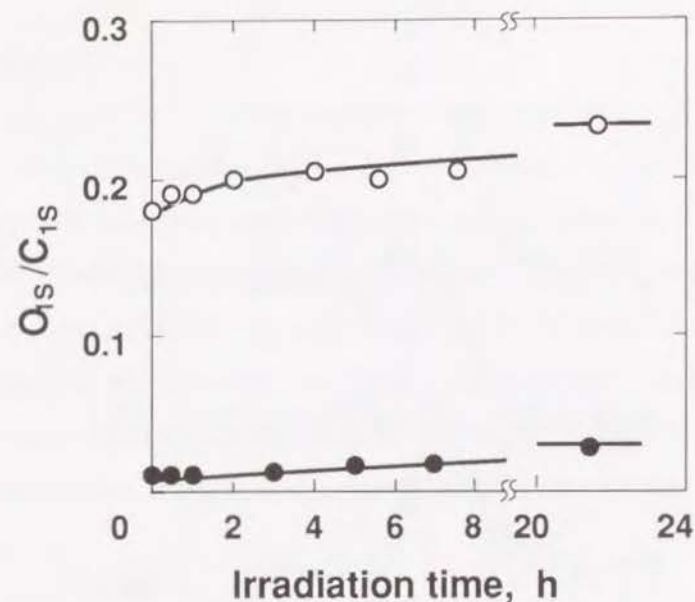


Fig. 3. Variation of O_{1s}/C_{1s} intensity ratio as a function of UV irradiation time: (○) nylon 6; (●) PP.

The O_{1s}/C_{1s} intensity ratios calculated from the integrated area of spectrum for nylon 6 and PP films are plotted against UV-irradiation time in Figure 3. For instance, the nylon film irradiated for 20 h has the O_{1s}/C_{1s} ratio higher than that of the unirradiated film by about 8%.

The peroxide yields of UV irradiated films are shown in Figure 4, where it can be seen that peroxides can be formed on the nylon and PP films by UV irradiation. The increase in peroxide concentration with the irradiation time is much larger than that of O_{1s}/C_{1s} ratio. This reason is not clear, but it seems that the different dependencies may be related to the difference in the depth below which the XPS or DPPH method is no more applicable. It is likely that the nylon 6 film is oxidized to the depth much deeper than 5 nm from the surface, when UV irradiation is prolonged.

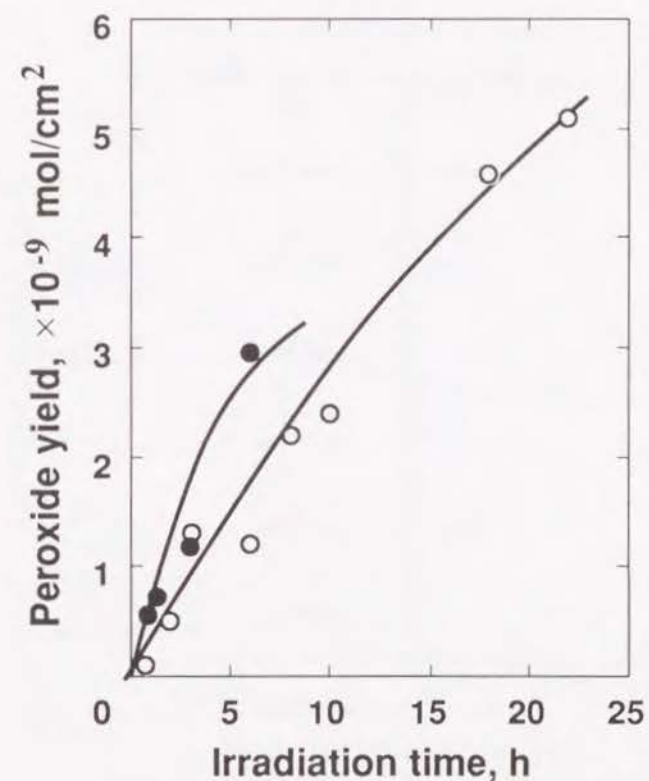


Fig. 4. Variation of peroxides yield as a function of UV irradiation time: (○) nylon 6; (●) PP.

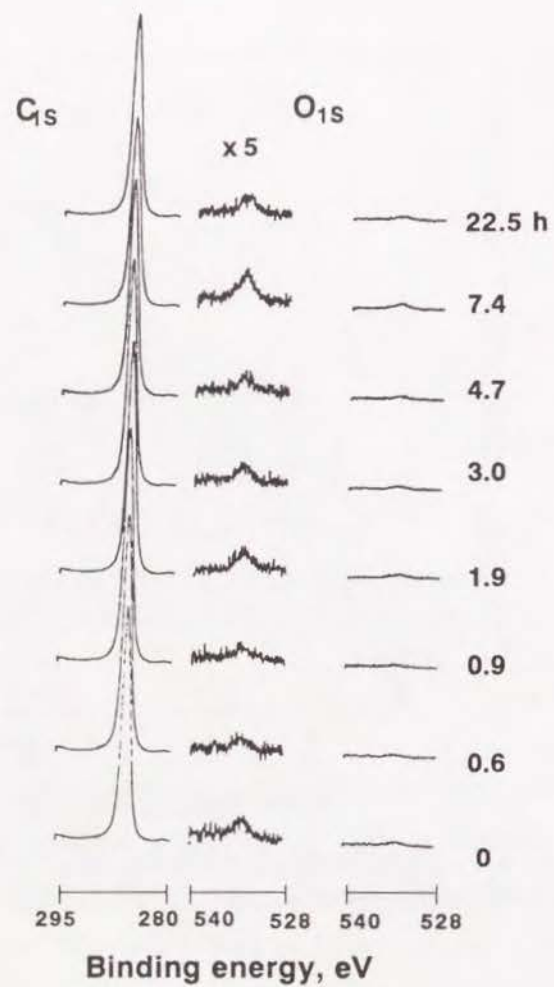


Fig. 5. C_{1s} and O_{1s} XPS spectra of polypropylene film untreated and exposed to UV radiation for different times.

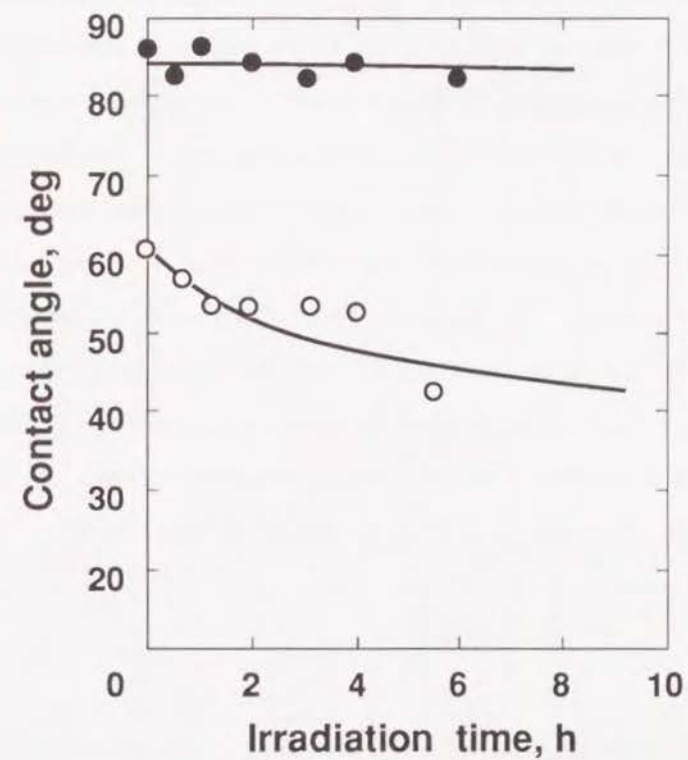


Fig. 6. Influence of UV irradiation time on the contact angle of films: (○) nylon 6; (●) PP.

This tendency is more obvious for the PP film irradiated for 20 h is only 0.3 %, while the peroxide formed on the PP upon irradiation has a yield higher than that for the nylon 6 film. XPS spectra of UV-irradiated PP films are shown in Figure 5.

UV light can probably penetrate through the PP polymer matrix more deeply than nylon 6, because pure PP does not absorb any light of UV wavelength range. According to Carlsson and Wiles[8], PP film undergoes photooxidation to 10^3 nm depth from the surface.

Expectedly, the UV-irradiated nylon 6 film became more wettable toward water than PP film. Changes of contact angle for nylon 6 and PP films are plotted against the UV-irradiation time in Figure 6. The contact angle is thought to be directly related to the properties of outermost surface layer of materials. The results in Figure 6 show the change of contact angles of UV-irradiated PP film to be much smaller than that for nylon 6 film, indicating that the hydrophilic groups such as peroxide group introduced on the surface of PP film is less than those for nylon 6. For both nylon 6 and PP films, no significant difference in transmittance of IR spectra was observed between the starting and the UV irradiated for 7.5 h. Figure 7 shows the example of IR spectra for PP film.

OTHER FILMS

The O_{1s}/C_{1s} intensity ratios calculated from the integrated area of spectrum for other films are plotted against UV-irradiation time in Figure 8, and the change of contact angles of UV-irradiated films are shown in Figure 9. In contrast to PP film, HDPE film which has high crystallinity and no tertiary carbon atoms in polymer chain, was less affected by UV radiation when analyzed with XPS and contact angle measurement. Pure polyethylene as well as PP has practically no oxygen atom in its molecule, whereas the small amount of oxygen was detected both for untreated HDPE and PP films as can be seen from Figures 3 and 8. It is probably due to the oxidation during the synthesis or manufacturing process of these films. PMMA is also known as one of the relatively stable polymers. For instance, Klesper et al.[10,11] reported that a vigorous condition is required for the hydrolysis of PMMA at room temperature. On the other

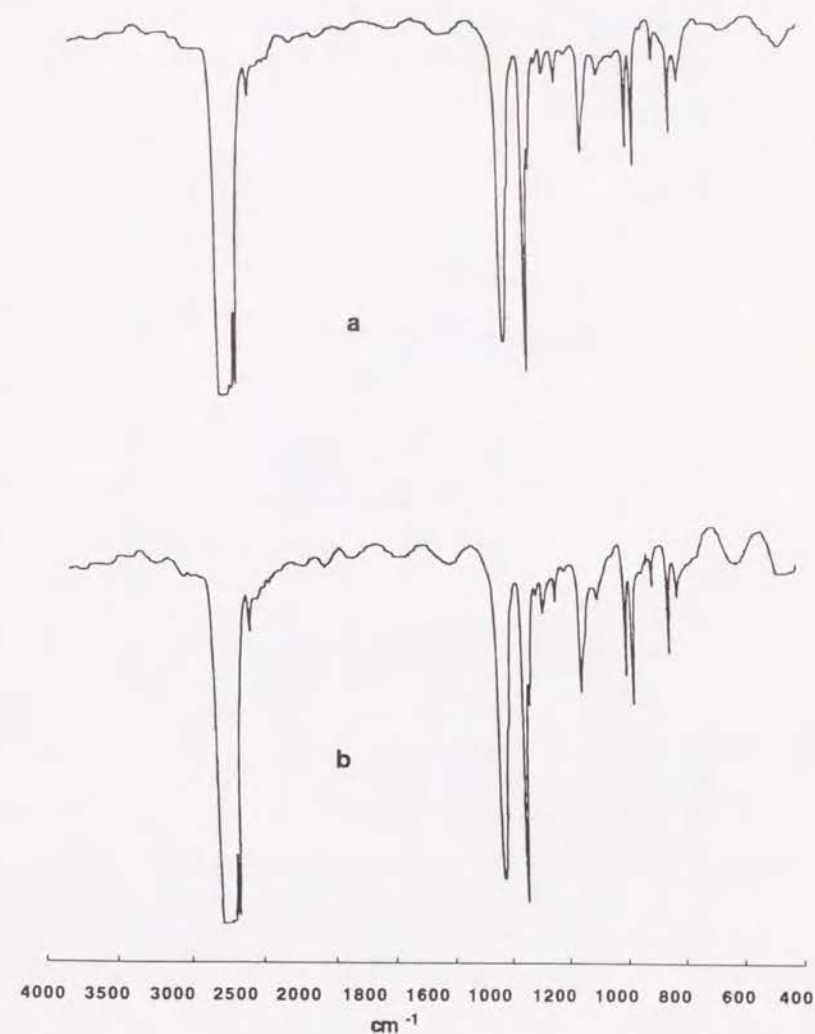


Fig. 7. IR spectra of polypropylene film untreated (a) and UV-irradiated for 7.5 h (b).

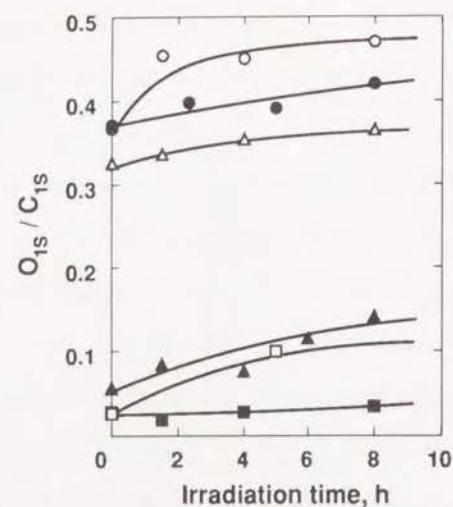


Fig. 8. Variation of O_{1s} / C_{1s} intensity ratio as a function of UV irradiation time: (○) PET, (●) PMMA, (△) VAECO, (▲) PVC, (■) HDPE, (□) PS.

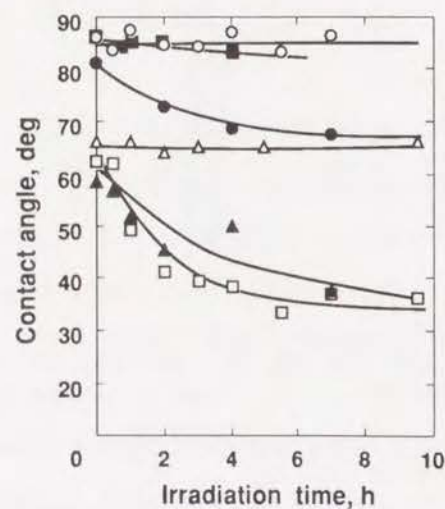


Fig. 9. Influence of UV irradiation time on the contact angle of films: (○) HDPE, (●) PVC, (△) PMMA, (▲) VAECO, (□) PET, (■) PS.

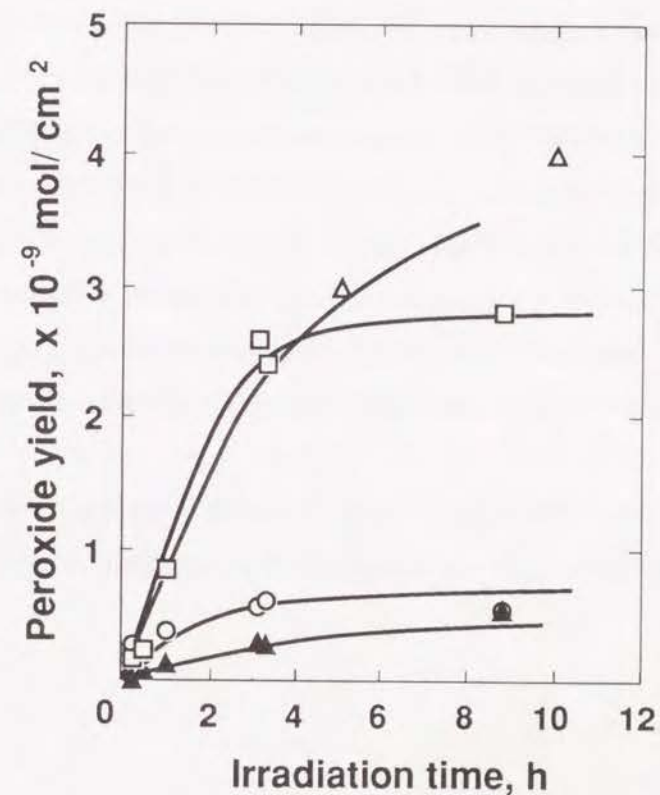


Fig. 10. Variation of peroxide yield as a function of UV irradiation time. (only the PMMA film was UV-irradiated with low-pressure mercury lamp): (○) HDPE, (△) PMMA, (□) PET, (▲) VAECO

hand, Yasuda[12] described the introduction of polar groups onto the PMMA surface with plasma treatment. As can be seen from Figures 8 and 9, PMMA was little influenced against oxidation with the exposure to UV light. In Figure 10, the peroxide yields determined by the DPPH method are given for films exposed to UV irradiation with a high pressure mercury lamp. Only the PMMA film was irradiated with a low-pressure mercury lamp (32 W Riko-32L type). As the effect of ozone is not negligible for the surface oxidation of polymers[13], UV irradiation was mostly performed using high pressure mercury lamp in the present work, which does not produce any significant amount of ozone. According to Ichijima et al.[14], the contact angle of PMMA hardly changed after exposure to high concentrated ozone-oxygen mixture. Figure 10 clearly shows that peroxide groups are markedly formed on the PMMA film by exposing to low-pressure mercury lamp which emits relatively low wavelengths of UV light. These findings suggest that, although PMMA is chemically stable against oxidation, it seems rather vulnerable to far UV light.

Similar to nylon 6 film, other polymer films, such as VAECO, PVC, and PS underwent rather easily photo-oxidation as can be seen from Figures 8 to 10.

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GRAFT POLYMERIZATION OF ACRYLAMIDE ONTO POLYMER FILMS

INTRODUCTION

Surface properties of polymers are often as important as their bulk properties. Therefore, there have been reported a variety of surface modification methods, including acidic or alkaline treatment, corona or flame exposure, polymer deposit or coating, metal vapor deposit or ion plating, additive blending, and so on. Polymer grafting has been also employed for the surface modification or functionizing of polymers. The methods investigated for the surface grafting involve either immobilization of polymer chains onto a polymer surface by coupling reactions[1] or graft polymerization of monomers via glow discharge[2,3], corona discharge[4], and irradiation with ionizing[5] or UV radiation.

The use of UV irradiation seems to be an excellent method because of the simplicity and cleanness of its treatment. Until now, most of the photoinduced graft polymerizations have been carried out with a simultaneous irradiation technique in the presence of photosensitizers[6,7]. As demonstrated in Chapter II, UV irradiation results in a build-up of hydroperoxides for many polymers, regardless of the presence of photosensitizers. These peroxides may become an efficient initiator for surface grafting, similar to irradiation with high energy radiation[5] and plasma treatment[3]. However, few work has been reported on the graft polymerization of monomers onto polymer surfaces which have previously been irradiated with UV radiation in the absence of photo-sensitizer. Rånby and his co-workers have reported UV-initiated surface grafting of a vinyl monomer onto polymer surfaces[9], but also their method is based on simultaneous irradiation of the substrate polymers in the presence of photoinitiators. This chapter will describe the results of graft polymerization of acrylamide (AAm) onto films such as nylon 6, polypropylene (PP), and ethylene-vinyl acetate copolymer (EVA).

EXPERIMENTAL

Films and Monomer

Films of nylon 6, PP, PE, EVA (VA content = 14, 19, and 28 mol%), and VAECO, (ethylene content = 33 mol%) were of commercial grade, mostly having a thickness around 20 μm . Purification of these films was carried out by Soxhlet extraction with acetone or methanol for 24 h. AAm monomer, of gel electrophoresis grade, was purified by recrystallization from the aqueous solution.

Graft Polymerization

UV irradiation of films was performed with a high-pressure mercury lamp (75 W, Toshiba SHL-100UV type, $\lambda > 254 \text{ nm}$) without any cutoff filter. Dried films were irradiated in air at ambient temperature by placing them 7 cm away from the center of the light source. Within 30 min after irradiation, graft polymerization onto the UV-irradiated films was carried out at 50°C with a deaerated aqueous solution of AAm at a concentration of 1.4 M. The polymerization time was kept to 1 h, unless otherwise noted. To remove the homopolymer from the grafted films, they were first washed with running tap water and then immersed in a distilled water kept at 70°C overnight under continuous stirring. The amount of polyacrylamide (PAAm) grafted was determined by measuring the absorbance at 570 nm for the solution obtained after complete hydrolysis of the grafted PAAm with 1.5 N HCl at 120°C and the subsequent reaction with ninhydrin[2].

RESULTS AND DISCUSSION

Graft Polymerization onto UV-Irradiated PP and Nylon

The amount of PAAm grafted onto PP films was plotted against the preirradiation time in Figure 1. Graft polymerization takes place in high yields with the increasing UV preirradiation time, in accordance with the results of XPS and DPPH measurement described earlier in Chapter II. It is likely that the graft polymerization was initiated by the radicals

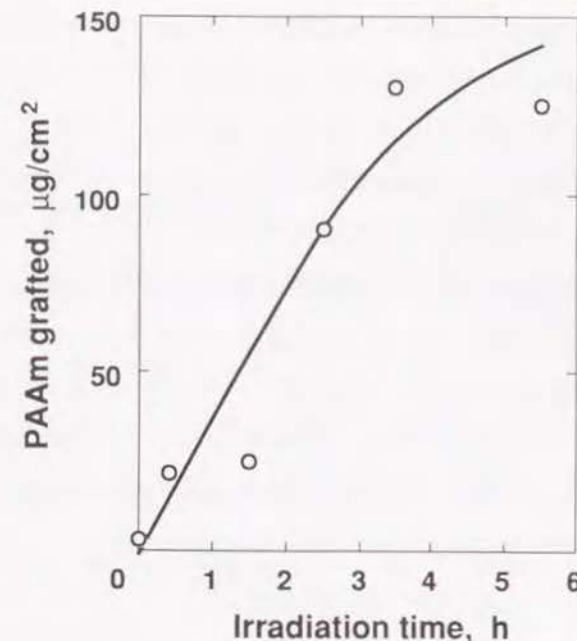


Fig. 1. Effect of UV irradiation time on graft polymerization of acrylamide onto polypropylene film.

generated upon thermal decomposition of the peroxides formed at and near the film surface with UV irradiation in air. Light microscopic observation revealed that only a limited layer of cross-section of PP film could be stained when the grafted PAAm was hydrolyzed to poly(acrylic acid) and then immersed in an aqueous solution of toluidine blue-O. Transmittance of AAm-grafted PP films at 640 nm was tabulated in Table I.

Graft polymerization of AAm altered the PP film surface from hydrophobic to hydrophilic and from nonlubricating to slippery surface. For instance, the contact angles of the PP films unirradiated and UV-irradiated for 5.5 h were 87 and 84°, respectively, whereas the film grafted to 120 $\mu\text{g}/\text{cm}^2$ had a contact angle as low as 21°. Graft polymerization of AAm onto the nylon 6 film preirradiated with UV took place as effectively as or more effectively than that for PP film. Unfortunately, amounts of PAAm grafted on nylon could not be determined with the ninhydrin method because of interference of amide bonds in nylon to the analysis. However, the nylon surface also became hydrophilic and slippery by the graft

polymerization. The contact angle of the nylon grafted with AAm after 5.5 h UV exposure was 22 and 42°, respectively. Over the range of the exposure time studied, UV irradiation had little effect both on the tensile strength and the elongation at break of the films as is shown in Table II. Also, SEM observation and IR measurement did not show any significant difference between the starting and the irradiated PP film.

There have been published numerous reports on photodeterioration or photooxidative degradation of polymer materials[10-13] especially of PP. This polymer has been found to be very vulnerable to photodegradation because of tertiary carbon atoms present in the polymer chain. Therefore, much effort has been made to prevent PP from degradation or to stabilize PP against UV exposure. The surface grafting using UV preirradiation studied above is an application of the active species generated upon UV irradiation in the early stage where polymer chain does not suffer significant cleavage yet.

Table I. Transmittance of acrylamide-grafted Polypropylene Films Stained with Toluidine Blue.

Pre-irradiation time, h	% Transmittance at 640 nm
0	100
0.4	42.1
1.5	23.7
2.5	1.6
4.0	0.6
5.5	0.1

Table II Effect of UV irradiation and graft polymerization of acrylamide on the mechanical properties of films.

Film	Tensile strength, 10 ⁵ kgcm ⁻²				Elongation at break, %			
	UV irradiation time, h				UV irradiation time, h			
	0	1.0	3.0	PAAm grafted	0	1.0	3.0	PAAm grafted
Nylon 6	6.1	5.70	5.81	5.79	392	422	404	435
PP	9.16	10.15	9.85	11.11	513	505	556	550

Grafting onto Other Polymer Films

EVA films having various vinyl acetate(VA) contents were used for surface grafting. The amount of PAAm grafted onto the preirradiated films was plotted against the preirradiation time in Figure 2. As is seen, graft polymerization takes place effectively also onto the EVA film irradiated with UV. The change of contact angle of the EVA film upon UV irradiation was small, independent of the VA content. For instance, the contact angles of unirradiated EVA films with VA contents of 14, 19, and 28% were 86, 84 and 85°, respectively, whereas those of UV-irradiated for 5 h were 81, 79, and 79°, respectively. However, the contact angle of the EVA films preirradiated for 4 h, followed by AAm grafting, became 10 to 15°, irrespective of the VA content.

Figure 3 shows the dependence of the amount of PAAm grafted on the VA content of the EVA film. It is clearly seen that EVA without VA component, that is, PE, is not grafted at all even under the prolonged irradiation (10 h), although a small amount of peroxides were detected as was discussed in Chapter II. The amount of PAAm grafted is not necessarily proportional to the amount of peroxides determined by the DPPH method. There are several factors influencing graft polymerization other than the peroxide yield. One of them

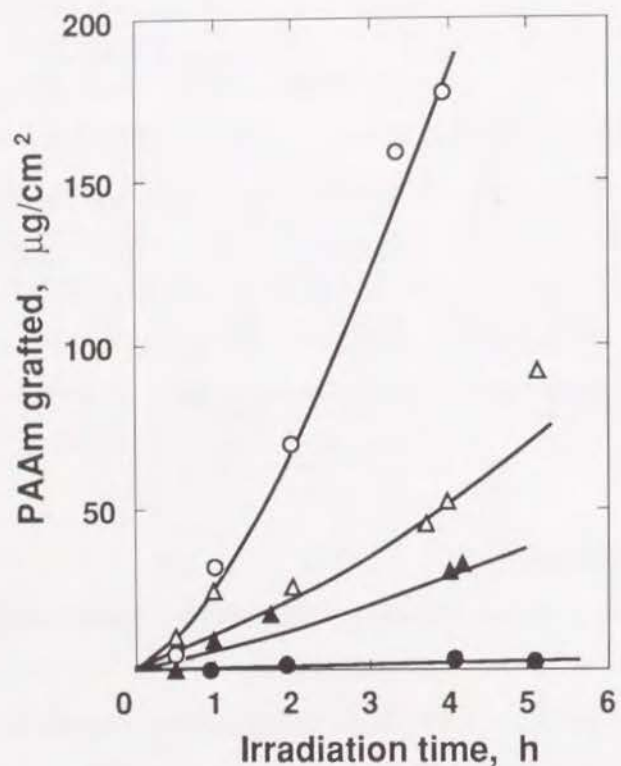
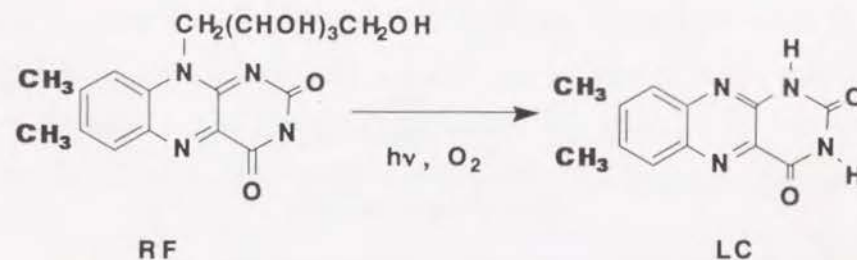


Fig. 2. Effect of UV irradiation time on graft polymerization of acrylamide onto polyethylene and ethylene-vinyl acetate copolymer films having various vinyl acetate contents: (●) VA 0% (PE); (○) VA 28%; (Δ) VA 19%; (▲) VA 14%.

is the permeability of monomer into the surface region of the irradiated polymer matrix. The monomer permeability depends not only on the glass transition temperature (T_g) of bulk polymer but on the hydrophilic property. In the case of VAECO film, which is relatively hydrophilic and has a low T_g , the PAAm grafted amounted to $450 \mu\text{g}/\text{cm}^2$ by preirradiation only for 1 h, whereas the amount of peroxides and the increase of O_{1s}/C_{1s} were not exceptionally large compared with those of other polymer films, as can be seen from Figures 8 and 10 in Chapter II. Any significant graft polymerization of AAm did not take place onto UV-irradiated, hydrophobic films such as silicone and polytetrafluoroethylene.

Grafting Without Degassing

Although the graft polymerization was successfully proceeded with the UV preirradiation method which seems relatively simple and clean, an obstacle still remains for graft polymerization in industrial applications, that is, the time-consuming degassing process. The most desirable way is to omit the oxygen removal process especially for surface graft polymerization on a large scale. A method for graft polymerization without degassing was extensively studied by Uchida et al. using sodium periodate[14]. It is also well known that riboflavin (RF, 6,7-dimethyl-1-(D-1'-ribityl)-isoalloxazine) undergoes photolysis to form lumichrome (LC, 6,7-dimethyl-alloxazine) consuming oxygen from the surrounding media[15-17].



To examine the role of riboflavin in consuming oxygen, pretreated films with UV radiation or other methods such as plasma treatment and ozonization was immersed to

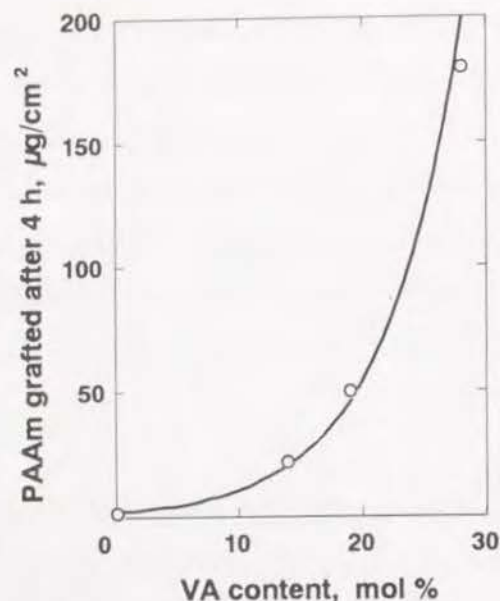


Fig. 9. Dependence of the vinyl acetate content on graft polymerization onto ethylene-vinyl acetate copolymer film preirradiated for 4 h.

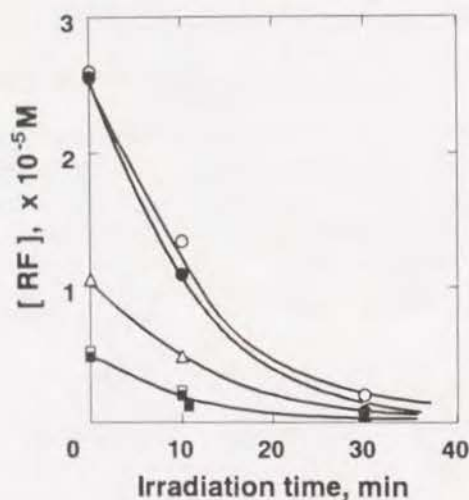


Fig. Variation of the concentration of riboflavin (RF) as a function of UV irradiation time. Open marks; aqueous riboflavin solution initially containing 2.6×10^{-5} M (○), 1.06×10^{-5} M (△), and 0.53×10^{-5} M (□). Filled marks; aqueous solution initially containing 2.6×10^{-5} M (●) and 0.53×10^{-5} M (■) in the presence of acrylamide (1.4 M).

aqueous monomer solution in the presence of small amounts of riboflavin. The Pyrex glass tube containing the mixture was then UV-irradiated from outside with a high-pressure mercury lamp, only sealing it with silicone stopper and without degassing procedure. Within 0.5 or 1 h of UV irradiation, graft polymerization of AAm onto these films took place as effectively as onto the films which received a degassing process without riboflavin. Although it is not the aim of the present study to get a whole understanding for the role of riboflavin, brief experiments were carried out as below. The concentration of riboflavin and oxygen in a solution was analyzed by measuring the optical density at 440 nm and using an oxygen electrode (DG type, Ishikawa Inc., Japan), respectively. The molar extinction coefficient of aqueous riboflavin solution obtained from the calibration of measurement was $1.2 \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1}$. It was found that the concentration of riboflavin decreased with the UV exposure time, simultaneously reducing the concentration of oxygen dissolved in the solution. For instance, variation of the concentration of riboflavin is plotted in Figure 4 against UV irradiation time for both the solution with monomer (acrylamide) and without monomer. It is clearly seen from Figure 4 that more than 90 % riboflavin was decomposed within 30 min of UV irradiation, regardless of the initial riboflavin concentration and no significant difference was found in the degree of removal of oxygen between the solution in the presence of monomer and in the absence of monomer. However, the decreasing rate of riboflavin seems to be somewhat enhanced with the existence of monomer.

It should particularly be noted in applying this degassing-saving method for surface graft polymerization that the presence of riboflavin not only contributes to the oxygen reducing in the solution but also retards the polymerization of monomer when excessive riboflavin remained in the reaction media without decomposing. It was found that polymerization did not start until riboflavin disappeared completely. This stage can be easily noticed with naked eye, because even a small amount of riboflavin exhibits clear yellowish color. When a monomer mixture containing high concentration of riboflavin was first completely degassed and sealed in Pyrex ampule, it neither changed its color nor polymerized even by prolonged radiation with UV for 3 h. On the other hand, the identical system with lumichrome instead of riboflavin enhanced greatly the graft polymerization. It is likely that

the existence of both oxygen and riboflavin prohibits polymerization and that lumichrome acts as a good photosensitizer for polymerization. It is necessary for this UV radiation method that both riboflavin and oxygen coexist in the initial stage and they should react each other with UV light leading to their complete disappearance in the stage of polymerization. The results obtained from grafting experiments in different reaction media using PET film pretreated with glow discharge is summarized in Table III. The appropriate concentration of riboflavin in the monomer solution was found to be around 10^{-5} M.

The graft polymerization without degassing process but with the use of riboflavin and UV-radiation seems to be promising, not only for the large-scale industrial applications but also for polymerization of monomers which have a lower critical solution temperature (LCST) such as N-isopropyl acrylamide monomer[18], because the effect of UV radiation is usually independent on the reaction temperature.

Table III The effect of riboflavin and lumichrome on photopolymerization of AAm onto PET.

System	Additive ^{a)}	Initial conc. x 10 ⁻⁵ M	Occurrence of polymerization ^{b)}	
			30 min	60 min
deaerated	RF	0	N	G
	RF	0.03	N	G
	RF	0.17	N	S
	RF	0.6	N	N
	RF	1.0	N	N
	RF	2.0	N	N
	LC	0.48	G	G
	LC	1.7	G	G
aerated	RF	0.03	N	N
	RF	0.6	N	S
	RF	1.0	G	G
	RF	2.0	S	G
	LC	0.02 - 1.7	N	N

a) RF; riboflavin, LC; lumichrome

b) N; not grafted, G; grafted, S; slightly grafted

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Chapter IV

ELECTROSTATIC PROPERTIES OF SURFACE-GRAFTED POLYMERS

INTRODUCTION

The generation of electrostatic charges on polymers has been mostly a nuisance in many fields associated with polymer and textile technologies. In addition to discomfort from static cling or static discharge, it often causes serious damage in semiconductor manufacture and sometimes to human life through fire or explosion. Therefore, it would be of great value to devise a simple method for eliminating static generation during manufacturing processes or to develop a new polymer that prevents charge generation. The mechanism for generation of the triboelectric charge is still controversial and it remains unclear whether the electric charge carrier is electrons, ions, or both. According to Montgomery and Loeb, the carrier might be electrons[1,2], whereas Harper states that the carrier is not entirely electrons if the charged material is strictly an insulator[3].

Whatever the mechanisms of charge generation are in an equilibrium process, it is possible to arrange materials in an electrostatic series such that any material in the series will become positively charged when brought into contact or rubbed with another material below it in the series[4,5]. According to Shaw and Hanstock[6], triboelectric charging is greatly influenced by the manner of rubbing. For instance, when quartz is rubbed hard with a silk, it becomes positive, whereas it becomes negative when brushed lightly with the silk. When similar pieces of an insulating material are rubbed together and the rubbing is inevitably asymmetric, there can be positive or negative charges, depending on the effect of friction on the two solid surfaces[7]. Henry[8] emphasized the importance of the temperature rise during rubbing, because the charge carrier would become easier to transport from one surface to the other at high temperatures.

Lowell and Truscott[9] studied the dependence of triboelectric generation on the friction speed. The higher the speed, the higher the temperature should become. However, contrary to Henry's observation, nylon and polytetrafluoroethylene were little influenced by the friction speed. It follows that the triboelectric charge generated on a polymer surface upon contacting or rubbing with another material cannot be identified absolutely. In addition, it should be noted that the charge is very unstable and depends on a variety of factors. For instance, the atmospheric conditions such as temperature and humidity will play a great role in the electrification of a surface[10]. As suggested above, both the magnitude and the sign of the electrostatic charge depend on the species of the opposing substrates, the pressure at contacting and rubbing, contaminants, the past history of the specimen, and so forth[11–14].

Regardless of the source, static charge is readily produced on polymeric materials having high electrical resistances when they are brought in contact with other solid surfaces, followed by separation or when they are placed in a high electric field. It is often difficult to dissipate their charges rapidly. Even highly conductive metals can be electrified under the same condition as polymeric materials, although their charge diminishes instantaneously if grounded. Many efforts have been made to minimize the electrostatic charging of polymer, mostly by rendering the polymer surfaces hydrophilic or electroconductive. The methods employed include surfactant mixing and metal fiber coveaving. Surface modifications of polymeric materials have been also studied in an attempt to reduce the generation of electrostatic charges[15–17]. The surface modification of polymers through grafting with the use of glow discharge[19], corona discharge, and irradiation with ionizing[20] and UV radiations[21] was already described. The purpose of this chapter is to study the electrostatic charging of surface-treated polymers. To this end, polystyrene and poly(ethylene terephthalate) films were irradiated with UV radiation and further surface-grafted with hydrophilic monomers. The electrostatic properties of these UV-irradiated and surface-grafted polymers were studied by charging through mechanical rubbing or exposure to high electric fields.

EXPERIMENTAL

Materials, UV Irradiation, and Graft Polymerization

Films of commercial grade polystyrene (PS) and poly(ethylene terephthalate) (PET) were prepared with a thickness around 30 μm . The films with a size of 5 x 5 cm^2 were purified by Soxhlet extraction with methanol for 20 h and then dried under reduced pressure. The purified films were stored in a desiccator kept at 25°C and 60 %RH, being placed between two filter papers. Fabrics of cotton and PET were used as received without purification.

UV irradiation of the films was performed with a high pressure mercury lamp (75W, Toshiba SHL-100UV type, $\lambda > 254 \text{ nm}$) in air at room temperature by placing them 7 cm from the center of the light source.

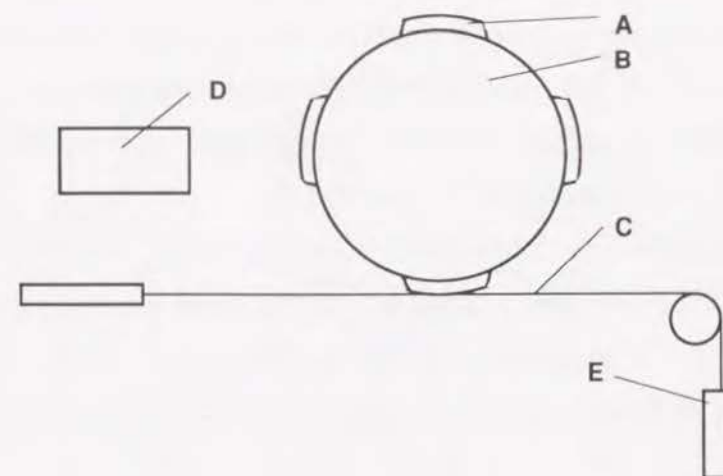


Fig. 1. Schematic representation of the apparatus used for determining the triboelectric charge generated upon rubbing with a cotton fabrics: A, specimen; B, rotary drum; C, cotton fabrics; D, detector; E, load.

The surface graft polymerization of various water-soluble monomers onto the PS and PET films and the PET fabrics was conducted according to the method described in Chapter III[22]. Briefly, a quartz glass tube containing the aqueous monomer solution in which the films or fabrics were immersed was irradiated with UV. The ungrafted homopolymer was extracted with boiling water.

Electrostatic Measurements

Triboelectric charges were generated on the polymeric materials and measured at 25°C and 60 %RH using a Rotary Static Tester (Kyodai Kaken type, Koa Shokai Ltd., Kyoto, Japan) by relatively gentle rubbing with the cotton fabrics for 30 s unless noted, because excessive rubbing might spoil the surface of the tested polymeric materials. The structure of the apparatus used is schematically illustrated in Figure 1. The test specimen(A) is fixed on a drum (B), which rotated at a rate of 540 rpm. As the diameter of the drum is 20 cm, the number of rubbings with cotton fabrics (C) is 540/min at a rate of 565 cm/s. The test specimen comes downwards on rotation and in contact with the cotton fabrics. The triboelectric charge generated is measured with a detector (D). A constant tension is applied to the cotton fabrics with a 500-g load (E). No significant difference in triboelectric charge was observed between the original cotton fabrics and the fabrics used after Soxhlet extraction with methanol. This indicates that there is no significant finish on the cotton fabrics. To perform measurements under the same conditions, the cotton to be used for rubbing was always replaced with a fresh one.

The rate of electrostatic decay was determined by measuring the half decay time, τ , of test specimens, which were initially charged to +5 kV or -5 kV by corona discharge, at 20°C and 75 %RH using a Static Honestmeter (Shishido Shokai Ltd., Tokyo, Japan). When it took too much time to determine the τ value, the percent of electrostatic charge still remaining after 3 min was determined.

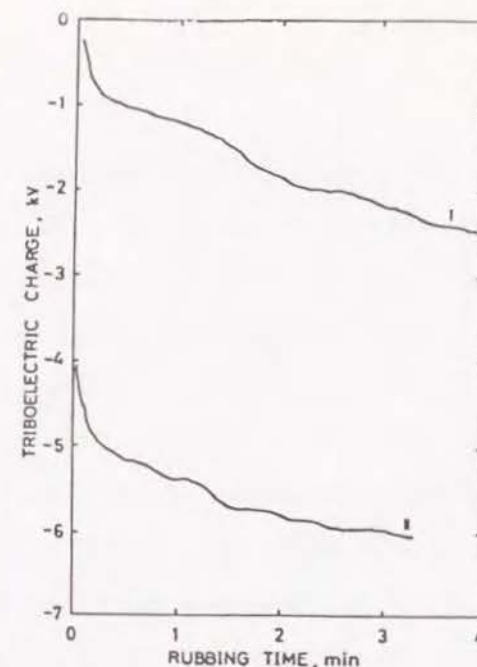


Fig.2. Triboelectric charge generated upon rubbing a polystyrene film with cotton fabrics. I, without any previous rubbing; II, after rubbing 5 times, each for 30 s.

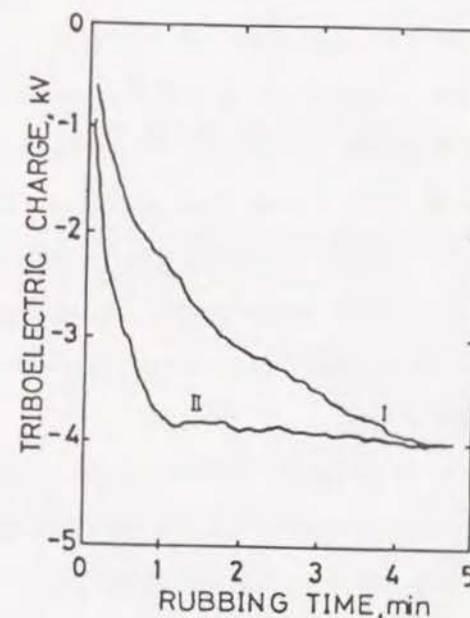


Fig.3. Triboelectric charge generated upon rubbing a poly(ethylene terephthalate) film with cotton fabrics. I, without any previous rubbing; II, after rubbing 5 times, each for 30 s.

RESULTS AND DISCUSSION

Unirradiated Films

As mentioned earlier, there are many complicating factors that influence the absolute value of a triboelectric charge generated on polymer surfaces. To minimize these complexities, it is necessary to measure the triboelectric charge of polymers under conditions as identical as possible for every measurement. The triboelectric charge generated on the unirradiated PS film is plotted against rubbing time in Figure 2, together with that for the PS film that had already undergone intermittent rubbing five times (a 30-s rubbing every 1h). As can be seen, the triboelectric charge of film that has experienced rubbing is much greater than for the freshly prepared starting film, reaching about -6 kV, although the rate of generation of triboelectric charge is almost the same for both films. However, it should be noted that the virgin PS film did not show any charge greater than -5 kV when rubbed continuously for 3 min, which corresponded to 3 s X 6 times. This may be due to temperature rise during continuous rubbing, because heating may make it easy for the charge carrier to transfer from the surface to the bulk or to the grounded equipment, resulting in a smaller amount of storage of electrostatic charge. This assumption is also supported by the fact that the triboelectric charge was always reduced when the contacting area of film and cotton fabrics was heated with an electric heater during rubbing. Watson[23] also studied the decay of surface electrostatic potential of a PS film at temperatures above and below the glass transition temperature (T_g). He concluded that, in the process of the transport of electrons from the surface into the bulk of PS, the decay is closely associated with the electron mobility and segmental motion in the rubber-like PS at temperatures above T_g . Below T_g , he concluded that the electrons remain frozen in traps in the polymer for an extremely long time. It is well known that polymer insulators such as PS retain their surface potential for a long period of time.

Figure 3 shows the result for the PET films. As can be seen, the difference in generated charge between the virgin and the rubbed films is much smaller than for the PS films. The rate of charge generation is also different. It is difficult to give clear explanation for this, but it

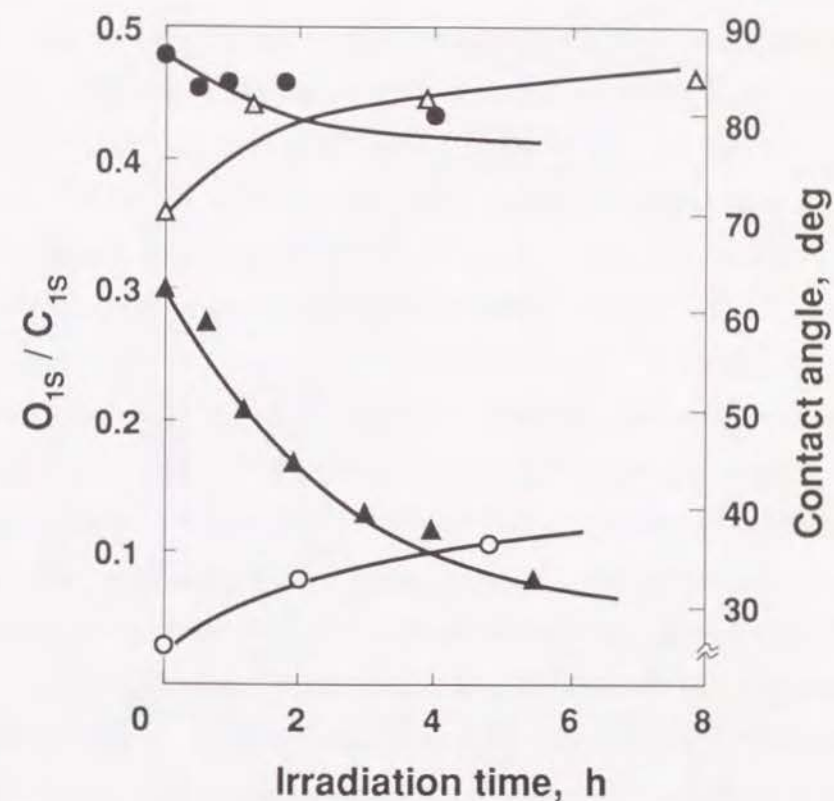


Fig. 4. Variation of O_{1s}/C_{1s} intensity ratio (open marks) and water contact angle (filled marks) as a function of UV irradiation time: $\circ$, $\bullet$, polystyrene; Δ , $\blacktriangle$, poly(ethylene terephthalate).

seems likely that the relatively high hydrophilicity of PET will promote discharging of accumulated charge carriers more than the less hydrophilic PS. The contact angle of the virgin PET film against water is 64° , while that of the virgin PS film is 87° .

UV-irradiated Films

As was shown in Chapter II, polymer surfaces undergo oxidation upon UV irradiation, resulting in more hydrophilic surfaces due to the generated polar groups. Figure 4 gives the O_{1s}/C_{1s} ratio obtained by an XPS study for the film surfaces, together with their water contact angles. It is seen that UV irradiation oxidizes the surface of PS and PET films, resulting in reduced water contact angles. Apparently, the PET film is more strongly oxidized by UV irradiation, as the reduction of contact angle takes place more markedly for the PET film than for the PS film.

The triboelectric charge generated on the UV-irradiated PS films upon rubbing is shown in Figure 5. The virgin and the UV-irradiated PS films were first rubbed only for 30 s. For the UV-irradiated PS films in particular, continued rubbing for longer periods of time was avoided because the surface suffered erosion by excessive rubbing. As described in Chapter II, the density of the polar groups introduced on the surface of PS film by UV irradiation seemed low compared with PET film. Actually, the surface of UV-irradiated PS film lost its hydrophilic character when rubbed repeatedly for periods longer than 30 min, suggesting that oxidation was limited to the surface region. The tested films were kept at 25°C and 60%RH for 1h and measurement was made in the same manner as for the first one after rubbing for 30 s. The previously rubbed films were further repeatedly rubbed for 30 s, after being kept for 2 h, 5 h, and 2 days after UV irradiation and the generated charge was measured. As is represented in Figure 5, the triboelectric charge apparently varied in a peculiar way with the UV irradiation time. The films irradiated for 1 and 2 h seem to be more susceptible to triboelectrification than the unirradiated and the films irradiated for longer than 2 h. However, as can be seen in Figure 5, the difference in the static charge between each step of rubbing is large for the unirradiated film and the films irradiated for 1 to 2 h, whereas UV irradiation for longer than 3 h induces an

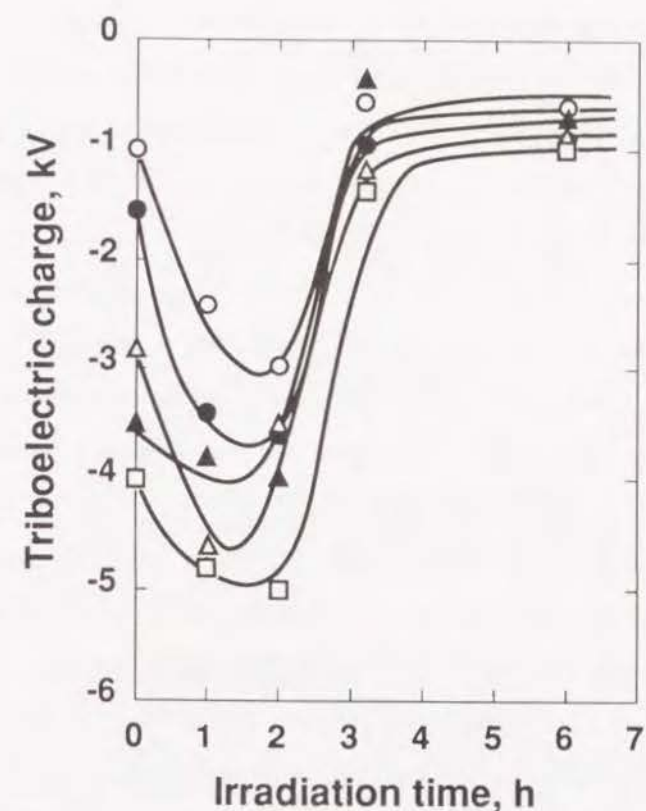


Fig. 5. Triboelectric charge generated upon rubbing UV-irradiated polystyrene films with a cotton fabric at 25°C and 60 % RH: O, measured immediately after UV irradiation; ●, 2nd after 1 h; Δ, 3rd after 2 h; ▲, 4th after 5 h; □, 5th after 2 days.

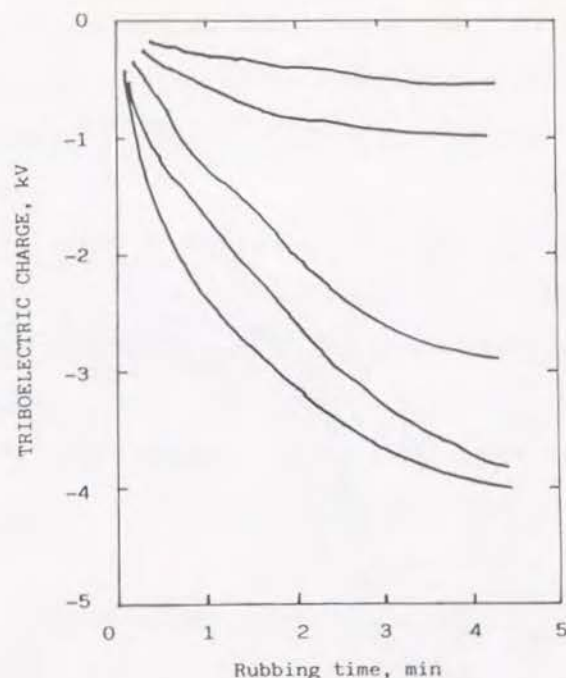


Fig. 6. Triboelectric charge generated upon rubbing a poly(ethylene terephthalate) film with cotton fabrics. number of rubs; 500 times per minute.

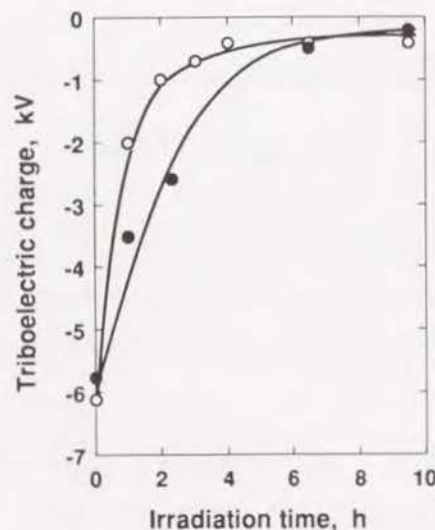


Fig. 7. Maximum triboelectric charge of UV-irradiated (○) polystyrene and (●) poly(ethylene terephthalate) films as a function of irradiation time.

insignificant charge difference between each rubbing step. This may be attributed to the different times to reach the maximal charge between the unirradiated and the UV-irradiated films. Sereda and Feldman[24] studied charging of various fabrics by rolling them between a nickel-plated roller and a nickel plate and found that the electrostatic charging on the fabric materials increased with the number of passes of the roller until it reached a maximum, and that the maximal charging was quickly achieved at higher relative humidity under formation of a monomolecular layer of water on the surface of materials. Referring to their results, the finding in Figure 5 may be explained as follows: the maximal charging is more readily reached when the surface becomes more hydrophilic by UV irradiation for 1 or 2 h, although the amount of hydrophilic groups introduced must be small, as expected from Figure 4.

For the UV-irradiated PET films, rubbing was conducted not intermittently but continuously because the maximum charging could be easily obtained, as can be seen from Figure 3, and no significant erosion of polar groups was observed for the UV- irradiated PET film.

The triboelectric charge of the PET films irradiated with UV radiation for different durations is shown in Figure 6. In contrast to the case of PS, PET films irradiated for longer periods of time always have a lower static charge when compared at the same rubbing time. This difference between the PS and the PET film may be ascribed to the different hydrophilicity of the starting films. As Figure 4 shows, the contact angle of virgin PS film is 87° , whereas that of PET is 64° . Thus, the PET surface may be more hydrated under the humidity of 60 %RH than the PS.

The maximum charge generated on the UV-irradiated PS film after a sixth intermittent rubbing is plotted in Figure 7, together with that of the UV-irradiated PET film, which was rubbed only once continuously for 3 min. As is clear, the maximal triboelectric charge is reduced with the irradiation time for both the films. Comparison of Figure 7 with Figure 5 reveals that repeated rubbing of the PS film further promotes the accumulation of electric charge.

However, it does not mean that the PS and PET films acquired improved properties as

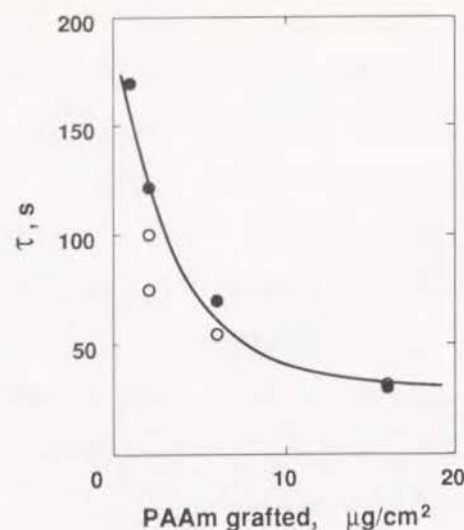


Fig. 8. Half decay time (τ) of grafted poly(ethylene terephthalate) films as a function of the graft density of polyacrylamide. The grafted film were initially exposed to electric fields of (○) +5 kV and (●) -5 kV.

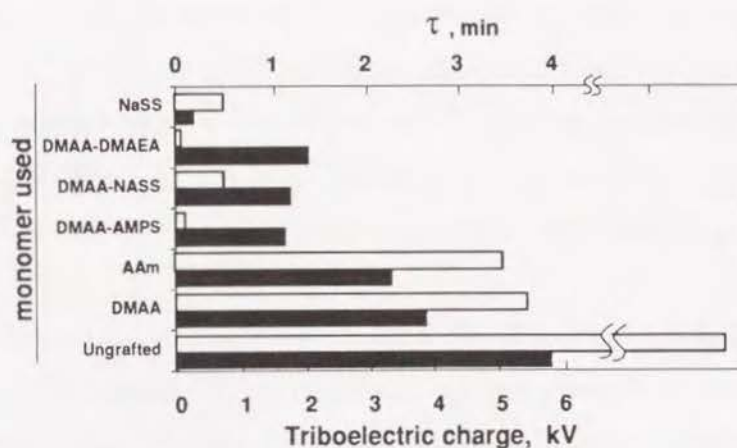


Fig. 9. Electrostatic properties of the poly(ethylene terephthalate) fabrics surface-grafted with various monomers. Triboelectric charge generated upon rubbing with a cotton fabric is given in absolute values neglecting the sign of the charge. Half decay time (τ) is the average of values observed when +5 kV and -5 kV were applied. Nass, sodium styrenesulfonate; DMAEA, N,N-dimethylaminoethyl acrylate; AMPS, 2-acrylamido-2-methylpropane sulfonic acid; □, half decay time; ■, triboelectric charge.

antistatic material by UV irradiation, because a low level of hydrophilic groups introduced by UV irradiation does not render the polymer surface conductive at all. Moreover, the UV-irradiated films did not exhibit any significant reduction in decay time of static charge, as is shown in Table I. The electrostatic charge generated by corona discharge did not decay to the half value even after 1 h. Only 2.7% of the charge disappeared after 3 min for the PS film irradiated for 5 h, although the initial charge was as low as -0.9 kV.

Table 1 Electrostatic Properties of UV-Irradiated and surface-Grafted Polymers

Specimen	UV irradiation time, h	Triboelectric charge ^a , kV	Half decay time ^b , s		% Decay ^b after 3 min	
			+5kV	-5kV	+5kV	-5kV
PS	0	-5.5	VL	VL	0.1	0.1
PS	1	-2.3	VL	VL	0.2	0.2
PS	2	-1.0	VL	VL	0.2	1.2
PS	5	-0.9	VL	VL	2.7	2.5
PET	0	-3.7	VL	VL	0.1	0.3
PET	1	-3.3	VL	VL	0.2	0.3
PET	2	-3.2	VL	VL	0.2	0.2
PET	5	-1.0	VL	VL	0.2	0.2
PET-g-DMAA	-	-0.5	18	21	78.0	80.0
PS-g-AA	-	-0.4	255	249	31.0	38.2

DMAA, N,N-dimethyl acrylamide; AA, acrylic acid.

^a 25° C, 60% RH

^b 20° C, 75 %RH, VL, very long (longer than 1 h)

The Surface-Grafted Materials

Most industrial films, plastics, and rubbers are hydrophobic and readily charged by rubbing. Since less hydrophobic materials are generally more difficult to charge, it seems interesting to study triboelectric charging of hydrophobic polymeric materials whose surface is grafted with

hydrophilic polymer chains. To examine the triboelectrostatic property of a hydrophilic polymer, a film of crosslinked poly(N,N-dimethylacrylamide)(PDMAA) was prepared by thermal polymerization of DMAA in the presence of a small amount of methylene bis-acrylamide as a crosslinking agent. The triboelectric charge of the obtained PDMAA film was dependent on the storage condition. When the film was thoroughly dried under a reduced pressure of about 0.1 torr prior to the charge measurement, the triboelectric charge was +0.9 kV, whereas film stored at 25°C and 60%RH for at least 1 week exhibited +0.02 kV as the triboelectric charge. This finding involves two different features: one is that even such a hydrophilic polymer as PDMAA is inevitably charged to about 1 kV by rubbing when completely dried and stored below 60%RH, and the other is that it may be possible to prepare an antistatic material through surface grafting provided the material is to be used under an ambient condition around 60 %RH.

PET film was graft-polymerized with DMAA by the photo-irradiation technique, as described in Chapter 3. The triboelectric charge of surface-grafted PET film is given in Table I. The charge generated upon rubbing at 25°C and 60 %RH is -0.5 kV and the half decay times, when +5kV and -5kV are initially applied, are as short as 18 and 21 s, respectively, in contrast to those of the UV-irradiated films. To determine the dependence of the electrostatic properties on the graft amount, the PET film was surface-grafted with acrylamide (AAm) since the amount of PAAm grafted was easily determined by the ninhydrin method. As can be seen from the results shown in Figure 8, the decay time is reduced considerably with an increasing amount of PAAm grafted. Unless water is present, neither hydrophilic polymers such as PDMAA nor surface-grafted polymers with hydrophilic monomers become conductive at all, contrary to the electroconductive polymers and the polymers blended with metals or carbon. However, the surface having a large amount of water-soluble graft chains will absorb plenty of water, when the surface is exposed to an environment of high humidity. The more hydrated surfaces will show lower decay times because the electric charge carriers may migrate more easily through the surface layer and be discharged more rapidly, as the surface is more hydrated.

If the graft chain possesses cationic or anionic groups, the surface-grafted material is

expected to become more effective in antistatic property. Results of triboelectrification and decay of charges are shown in Figure 9 for the PET fabrics that were surface-grafted with various water-soluble monomers. The monomers employed for the surface graft polymerization onto the PET fabrics include sodium styrenesulfonate and 2-acrylamido-2-methylpropane sulfonic acid as anionic monomers and dimethylaminoethyl methacrylate as cationic monomer in addition to nonionic monomers (DMAA and AAm). When graft polymerization of a single monomer was difficult, equimolar mixtures of two different monomers were used for graft polymerization. The half decay time of the ungrafted PET fabrics was around 1.5 h. Figure 9 indicates that electrostatic charging is more strongly inhibited by graft polymerization of ionic monomers than of nonionic ones. However, one cannot give an answer to the question of which monomer, anionic or cationic, is more appropriate for reducing electrostatic charging. A more detailed study is needed to get a deeper insight into the triboelectrification of surface-grafted films and fabrics.

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Chapter V

ADHESION BETWEEN FILMS SURFACE-GRAFTED WITH WATER-SOLUBLE MONOMERS

INTRODUCTION

Conventionally, adhesion is achieved by applying adhesives to substrates to be adhered and the subsequent solidification of the liquid-like adhesives results in a strong bond between the substrates. It is theoretically possible to achieve adhesion without applying any adhesives to the substrates. Indeed, as previously demonstrated[1], two polymer substrates could be adhered without any adhesives if their surfaces possessed chemically reactive groups which would form covalent bonds between them when brought into close contact.

It was found that a polymer surface modified by graft polymerization of water-soluble monomers, such as acrylamide (AAM), becomes simultaneously very hydrophilic and lubricious and slippery when wetted with water, although an insignificant difference is observed between the grafted and the ungrafted surfaces when dried[2]. In addition, the grafted polymer surface shows substantial adhesion to another surface when brought into contact in the presence of water and subsequently dried.

The study to be described in this chapter was undertaken in an attempt to investigate the adhesion of grafted surface to other substrates with different wettability without applying any adhesives. For this purpose, the surface of a poly(ethylene terephthalate)(PET) film was graft-polymerized with water-soluble, nonionic and ionic monomers by a photoradiation technique[3] in the presence of riboflavin without degassing procedure after plasma treatment[4]. Riboflavin consumed the oxygen molecules present in the monomer solution upon UV irradiation[5]. Plasma treatment was undertaken to introduce hydroperoxides on the film surface which was broken in the subsequent UV irradiation and initiated graft polymerization. The adhesion force between two polymer films was measured after being

contacted with water, and lapped together under a load. The films were then allowed to dry up.

EXPERIMENTAL

Film and Monomers

The PET film was of commercial grade, having a thickness of 50 μm . Purification of the film was performed by Soxhlet extraction with methanol for 20 h before use. The AAm monomer of gel electrophoresis grade was purified by recrystallization from an aqueous solution. An anionic monomer, acrylic acid(AAc), and a cationic monomer, N,N-dimethylpropyl acrylamide (DMPAA), were both purified by conventional distillation.

Glow Discharge

A glow discharge reactor, Model LCVD-12 type manufactured by Shimadzu Corp., Kyoto, Japan, equipped with a bell-jar-type reaction cell, was used for the plasma pretreatment of the PET film. The film was fixed to a stainless steel sample holder placed between two electrodes, to which RF power was applied at a frequency of 5 KHz. The holder was rotated at 68 rpm by a motor to ensure homogeneous plasma treatment over the whole film surface. The pressure in the bell jar was first reduced to 10^{-3} torr or lower, and subsequently Ar gas was introduced at a flow rate of about 20 ml/min. When the pressure in the bell jar was maintained at about 0.03 torr of Ar, the films were subjected to glow discharge mostly for 10 sec, unless otherwise noted. These Ar plasma pre-treated films were then exposed to dry air prior to grafting.

Graft Polymerization

Following the plasma treatment, the PET film was placed in a Pyrex test tube, together with a monomer solution, to which a small amount of riboflavin (10^{-5} M) was added. To effect graft polymerization, the mixture was kept at 40°C without degassing procedure and

irradiated by a high-pressure mercury lamp (1 kW, Riko-1000 HL type) at a distance of 10 cm from the tube for 1 h. Care was taken for the film to be homogeneously irradiated by the UV source so as to be photo-grafted homogeneously onto the surface. To remove the homopolymer formed, the grafted film was first washed with running tap water and then immersed in distilled water at 70°C for 20 h under continuous stirring. The surface density of AAm polymer grafted was determined quantitatively by the ninhydrin method, as described elsewhere[6]. The graft density of ionic polymers was determined by gravimetry or with a dye method[7].

Contact Angle and Zeta Potential Measurements

The surface hydrophilicity of the grafted films was evaluated by measuring their contact angle against water at 25°C and 65 %RH with a sessile drop method[8] using a 3 μL water droplet in a telescopic goniometer(M2010A-6II type, Elma Inc., Tokyo). The telescope with a magnification power of 40 X was equipped with a protractor of 1° graduation. At least four measurements on different surface locations were averaged. The scattering of reading was $\pm 4^\circ$. The zeta potentials of films were calculated from their streaming potentials measured at pH 7.4 and the ionic strength of 6.3×10^{-3} .

Adhesion Force Measurement

The adhesion force between two different film strips was determined with the aid of a tensile testing machine, after the two strips were lapped together and brought into close contact under a constant load of 18.1N, keeping the contact area to $10 \times 5 \text{ mm}^2$ in the presence of distilled water, unless otherwise specified. Figure 1 illustrates the arrangement of the sample films tested. The shear strength was measured at a crosshead speed of 10 mm/min as a function of time immediately after lapping the two different strips. In the following, the term "adhesion time" will be used without distinguishing from the drying time which was performed at 25°C and 65%RH throughout the present study.



Fig. 1. Schematic representation of lapping of two pieces of films to measure the shear strength.

RESULTS

Surface Graft Polymerization

The plasma-pretreated and the grafted surfaces became hydrophilic in comparison to the virgin PET film. The results of contact angle measurements for the surface-modified films are presented in Table 1, together with the graft density and the zeta potential. As can be seen, the PET film became hydrophilic by glow discharge alone, but a more remarkable decrease in contact angle was observed when grafted with AAm and AAc polymers. On the other hand, the DMAPAA-grafted films were still hydrophobic, whereas the plasma-pretreated film became hydrophilic, presumably by physical dense adsorption of small ions like OH^- and Cl^- . Although zeta potentials of virgin and Ar plasma treated films exhibited large negative charges, those of AAC- and DPAPAA-grafted films clearly showed

Table I Water contact angles and zeta potentials of surface-modified PET films^{a)}

surface	Graft density ($\mu\text{g}/\text{cm}^2$)	Contact angle (deg.)	Zeta potential (mV)
Virgin	0	61	-50
Ar plasma ^{b)}	0	44	-48
AAm-grafted	30	22	-0.4
AAm-grafted	90	24	
AAc-grafted	4	35	
AAc-grafted	52	34	-27.3
AAc-grafted	84	24	
DMAPAA-grafted	<1	75	
DMAPAA-grafted	8	60	+17.0

a) Films with various graft densities were prepared for comparison.

b) 10 sec exposure

different values, indicating that both surfaces were actually grafted with AAc and DMAPAA polymers, having negative and positive fixed charges, respectively. The contact angle of AAm- and AAc-grafted surfaces is seen to be almost independent of the graft density when it exceeds $30 \mu\text{g}/\text{cm}^2$, probably because of coverage of the entire PET surface by the graft chains.

Adhesion

The adhesion force between two grafted films strongly depended on the contact area. Table 2 gives a typical result of maximum shear force at break measured after a given period of drying(adhesion) time for films having two different contact areas(10×5 and $6 \times 3 \text{ mm}^2$), together with the shear strengths per unit area and the ratios of the two shear strengths. Apparently, the shear force between the films of larger contact area was always higher than that of smaller one, but the ratio of shear strengths per unit area depended on the drying time. In the initial stage of adhesion, the films of larger contact area had higher strength. In the middle stage, the rate of drying will become more influential on the adhesion. Rapid drying is apparently difficult for the larger contact area, because the substrate polymer is impervious.

However, in the final stage of drying, adhesion became more complicated, primarily resulting from the increasing sites of failure in adhesion. Therefore, the adhesion force was always determined at a fixed contact area of $10 \times 5 \text{ mm}^2$ in the following measurements.

1. Adhesion of AAm-Grafted Surface

Time dependence of the shear strength of an AAm-grafted PET film against different kinds of polymeric surface is shown in Figure 2. The AAm-grafted film had a graft density of $90 \mu\text{g}/\text{cm}^2$. As can be seen, the adhesion strength increases monotonously with increasing adhesion time for all the opposing surfaces. The leveling-off shear strengths are plotted against the water contact angles of opposing polymer surfaces in Figure 3. It is seen that stronger adhesion is achieved when the opposing surface is more hydrophilic. Sumiya et al. also studied the dependence of the polar component of surface energy of adherends on the adhesion force and showed that the shear strength increased linearly with the increasing surface energy[9]. It is interesting to note that when the same AAm-grafted film is

Table II Effect of the contact area on the adhesion between two AAm-grafted PET films.

Graft density $\mu\text{g}/\text{cm}^2$	Adhesion time min	Shear force (N)		Tensile shear strength(N/cm^2)		Strength ratio ^{a)}
		$10 \times 5 \text{ mm}^2$	$6 \times 3 \text{ mm}^2$	$10 \times 5 \text{ mm}^2$	$6 \times 3 \text{ mm}^2$	
55	5	1.1	0.2	2.2	0.9	0.4
55	10	1.2	0.3	2.3	1.4	0.6
55	30	12.5	5.9	25.0	33.0	1.3
55	60	14.9	11.1	29.8	61.4	2.1
55	1080	28.4	9.7	56.7	53.9	1.0
90	3	1.4	0.1	2.7	0.7	0.3
90	10	2.8	0.9	5.5	5.1	0.9
90	35	13.7	16.1	27.3	89.6	3.3
90	60	23.3	20.9	46.6	116.1	2.5
90	1080	40.6	7.4	81.2	41.3	0.5

a) ratio of shear strengths per unit area determined for two different contact areas

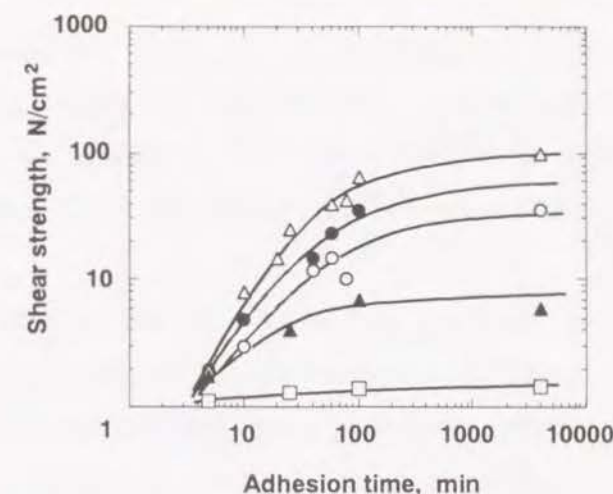


Fig. 2. Time dependence of the shear strength between an acrylamide(AAm)-grafted poly(ethylene terephthalate) (PET) film ($90 \mu\text{g}/\text{cm}^2$) and another film. (○) Virgin PET film; (●) PET film treated with Ar plasma for 10 s without grafting; (△) AAm-grafted PET film ($90 \mu\text{g}/\text{cm}^2$); (▲) low-density polyethylene; (□) polytetrafluoroethylene.

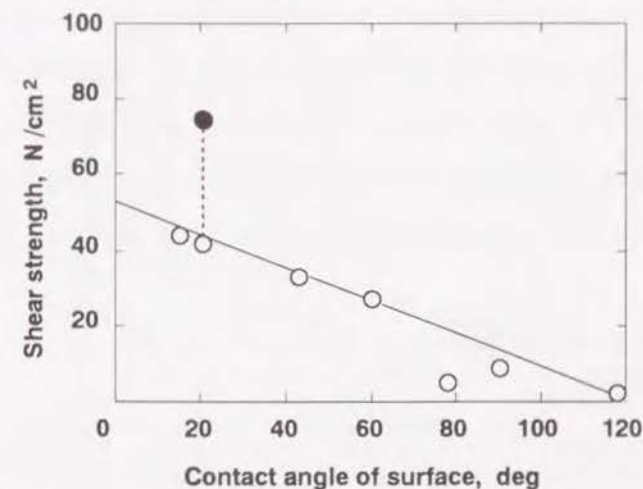


Fig. 3. Influence of the water contact angle of the opposing surface on the shear strength observed when contacted with an acrylamide(AAm) grafted poly(ethylene terephthalate) (PET) film ($90 \mu\text{g}/\text{cm}^2$). The shear strength observed when the opposing surface is the same as AAm-grafted PET is shown by a closed circle.

employed as the opposing film, the shear strength is very high and clearly deviates from the strength–contact angle relation for other non-grafted surfaces. A poly(vinyl alcohol) (PVA) film and a plasma-treated low-density polyethylene(PE) film were also used as the opposing films for adhesion with the AAm-grafted PET film, but the shear strength could not be determined, because the PVA and plasma-treated PE films themselves underwent rupture before adhesion failure.

Figure 4 shows logarithmic plots of the shear strength between two identical AAm-grafted films with different graft densities against the adhesion time. It appears that the graft density does not have a large effect on the adhesion strength, as long as it is larger than $10 \mu\text{g}/\text{cm}^2$. However, closer inspection of the results reveals that the film having lower graft density exhibits higher shear strength in the initial stage of drying, but has a lower leveling-off shear strength. This effect of graft density suggests that the adhesion force is significantly governed by the water content in the grafted layer. Therefore, the drying rate of water present at the interface of two AAm-grafted films was determined by measuring the weight decrease of two lapped wet films. Figure 5 shows the result of AAm-grafted films with two different graft densities and hence water contents. As is clearly seen, the drying rate of the film with the higher graft density is low both in the initial stage (within 10 min) and in the late stage (after about 100 min). The increase in adhesion force also slowed down from 100 min onward, as can be seen from Figure 4. In the case of the film with the lower graft density, the initial retardation of drying was hardly observed.

2. Adhesion between Ionic Surfaces

2.1. Anionic–anionic pair

Figure 6 shows time dependence of the adhesion force between two identical AAc-grafted films. The graft density of the film is $190 \mu\text{g}/\text{cm}^2$. Apparently, very weak adhesion is obtained in the initial stage of drying, but the shear strength steeply increases after 30 min and approaches $60 \text{ N}/\text{cm}^2$. Therefore, one can say that the shape of adhesion curve between two anionic surfaces is quite different from that between two nonionic surfaces such as shown in Figure 4, at least, in the initial stage of adhesion.

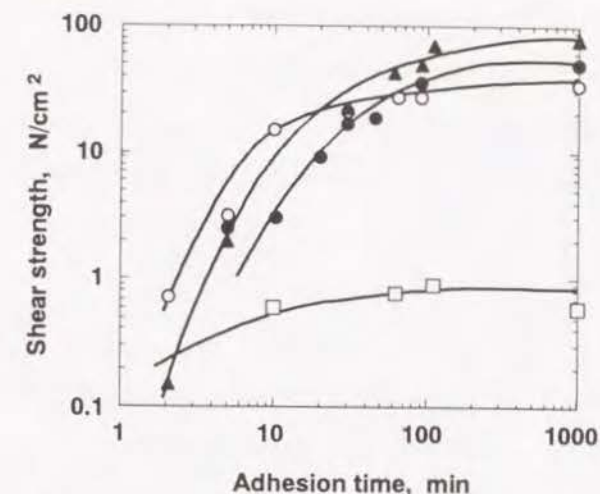


Fig. 4. Effect of the graft density on the shear strength between two identical acrylamide-grafted poly(ethylene terephthalate) films. Graft density ($\mu\text{g}/\text{cm}^2$): ($\square$) 1; ($\circ$) 10; ($\bullet$) 50; ($\blacktriangle$) 90.

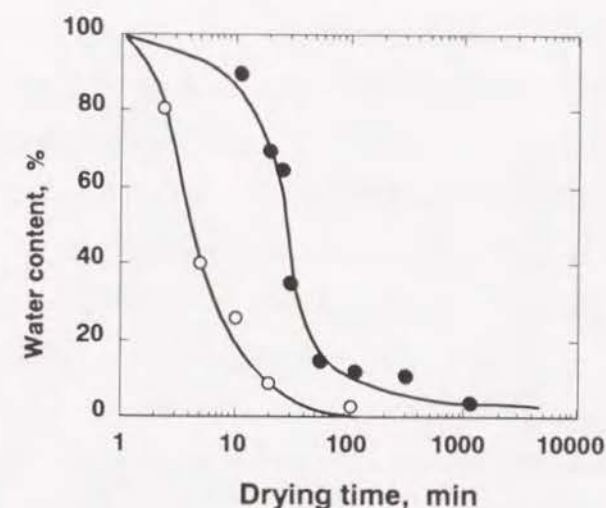


Fig. 5. Decrease in the relative water content for two lapped, wet acrylamide-grafted films as a function of the drying time. Initial water content (mg/cm^2): ($\circ$) 0.2; ($\bullet$) 14.5. Graft density ($\mu\text{g}/\text{cm}^2$): ($\circ$) 1; ($\bullet$) 90.

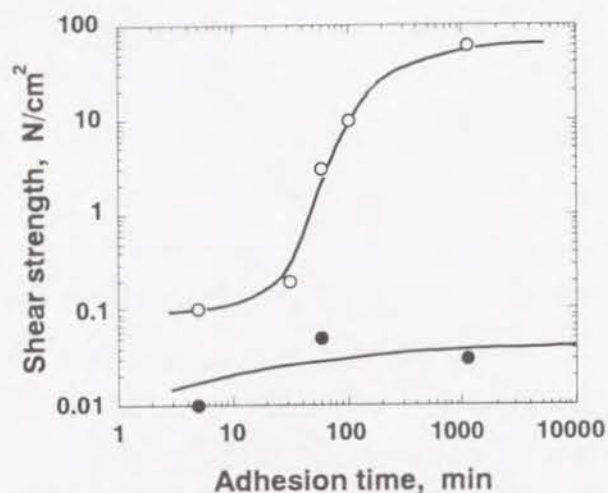


Fig. 6. Shear strength between two identical ionically grafted surfaces. (○) Anionic(AAc, $190 \mu\text{g}/\text{cm}^2$); (●) cationic(DMAPAA, $8 \mu\text{g}/\text{cm}^2$).

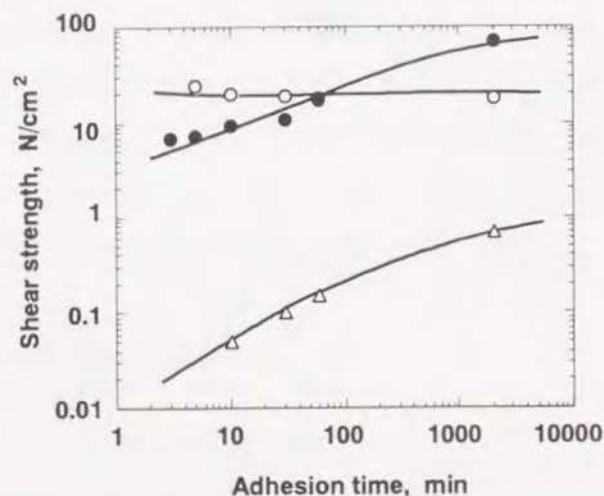


Fig. 7. Shear strength between an acrylic acid(AAc)-grafted film and a DMAPAA-grafted film wetted with distilled water or 0.2 M NaCl. (○, ●) Distilled water; (Δ) 0.2 M NaCl Graft density, AAc/DMAPAA: (○, Δ) 4/8; (●) 190/8.

2.2. Cationic-cationic pair

The time course of adhesion between two identical DMAPAA-grafted films is also shown in Figure 6. The graft density is as low as $5 \mu\text{g}/\text{cm}^2$, because of the difficulty in the surface graft-polymerization of this cationic monomer. As is seen, contrary to the anionic surface, this cationic surface does not exhibit substantial adhesion even after drying for 500 min. This is rather reasonable because the surface was practically not wettable.

2.3. Anionic-cationic pair

When an AAc-grafted film was brought into contact with a DMAPAA-grafted film under a load, the films adhered with each other almost instantaneously. The time dependence of shear strength for this pair with various graft densities is shown in Figure 7. As it was technically not possible to determine the precise strength of adhesion at time zero with our tensile testing machine, the shear strength was determined 3 min after contact. It is seen that the adhesion between the AAc-grafted film with a graft density of $4 \mu\text{g}/\text{cm}^2$ and the DMAPAA-grafted film with a graft density of $8 \mu\text{g}/\text{cm}^2$ yields shear strength as high as $15 \text{ N}/\text{cm}^2$ already at the moment of films contact, whereas a somewhat smaller adhesion force is obtained for the AAc-grafted film with a graft density of $190 \mu\text{g}/\text{cm}^2$ and the DMAPAA-grafted film with a graft density of $8 \mu\text{g}/\text{cm}^2$ pair in the initial stage of adhesion, probably because of the presence of plenty of water molecules at the AAc-grafted layer. However, the shear strength in the early stage is clearly much higher for both cases than that of nonionic(AAm)-nonionic(AAm) pair shown in Figure 4.

As is well known, the ionic interaction between the charged groups in aqueous media is greatly influenced by the presence of salts. The salt effect on the adhesion studied using 0.2 M NaCl as the medium is also shown in Figure 7. Expectedly, the shear strength remarkably decreased in the presence of NaCl.

After completion of the adhesion test on the anionic-cationic pair in distilled water, the used films were subjected to the second measurement of shear strength conducted in the same manner as the first measurement. Two examples of the result are shown in Figure 8. As can be seen, the second and the third measurement showed remarkably weak adhesion

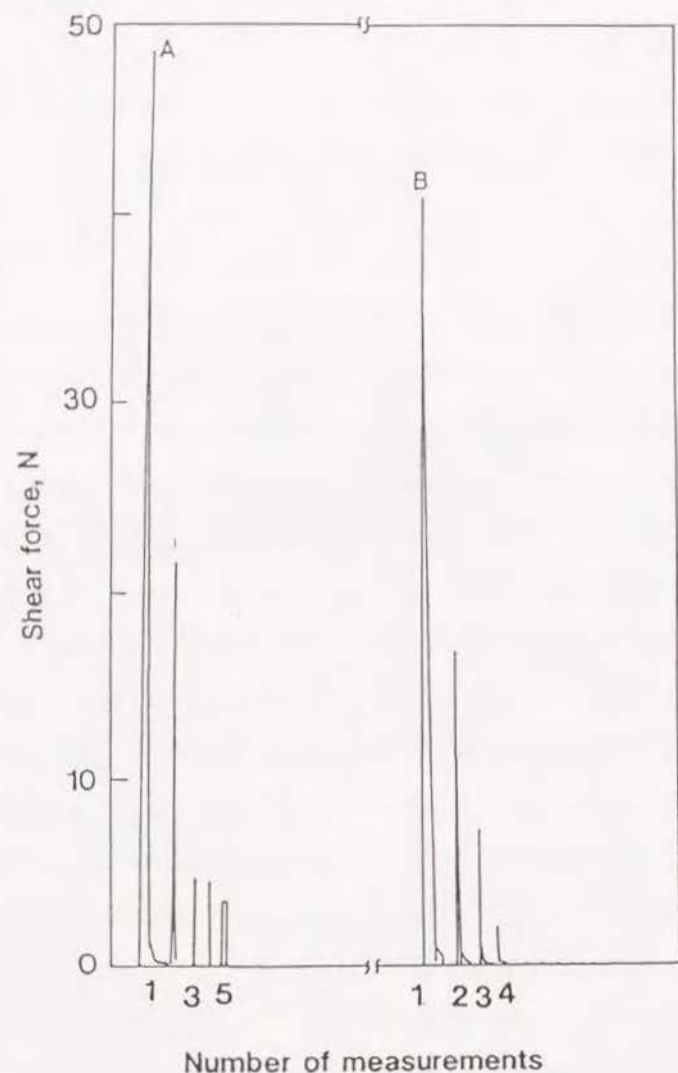


Fig.8 Repeated measurements of the adhesion force between an AAc-grafted and a DMAPAA-grafted film using the identical films after adhesive experiment. The initial graft densities were 4 and 8 $\mu\text{g}/\text{cm}^2$ for AAc and DMAPAA, respectively, and two series of experiment(A and B) were carried out.

compared to the first measurement, probably due to partial removal of the graft chains from the polymer substrate, but some strength was still observed even at the fourth and fifth measurements.

Although all the measurements of shear strength were performed in every pair of films at 25° C and 65%RH, it should be noted that no significant difference in strength was observed even when the dried films were placed in high moisture environment of 85%RH and 25° C prior to measurement.

DISCUSSION

The exact physical structure of the substrate surface grafted with polymer chains through surface graft polymerization is not yet clear. It is likely that a small fraction of graft chains are mixed with the substrate polymer chains to form a thin mixed layer at the substrate surface region, as proposed in previously[10]. For simplicity, we will represent the structure of grafted surface before drying as schematically illustrated in Figure 9(a). The graft chains are swollen with the solvent. In the present case, the substrate is a PET film and the graft chains are water-soluble polymers from AAm, AAc or DMAPAA. The solvent employed is distilled water except in one case where 0.2 M NaCl was used.

If such a surface-grafted film is brought into contact with another film in the presence of water, the graft chains will function as adhesives when the water disappears from the interface by simple diffusion or evaporation. With the decreasing content of water, an effect due to increased amount of interfacial bonds would be dominated. If the opposing film also possesses graft chains on the surface, chain entanglement between the polymer molecules belonging to the different substrates will take place to same extent, as illustrated in Figure 9(b), as long as no repulsive force is operative between them. The interaction between the oppositely charged surfaces is depicted in Figure 9 (c).

This assumed mechanism seems to be in accordance with the results presented above. For instance, the AAm-grafted PET film developed strong adhesion giving a shear strength as high as 100 N/cm^2 when two identical films were hydrated, lapped under a load of 18 N,

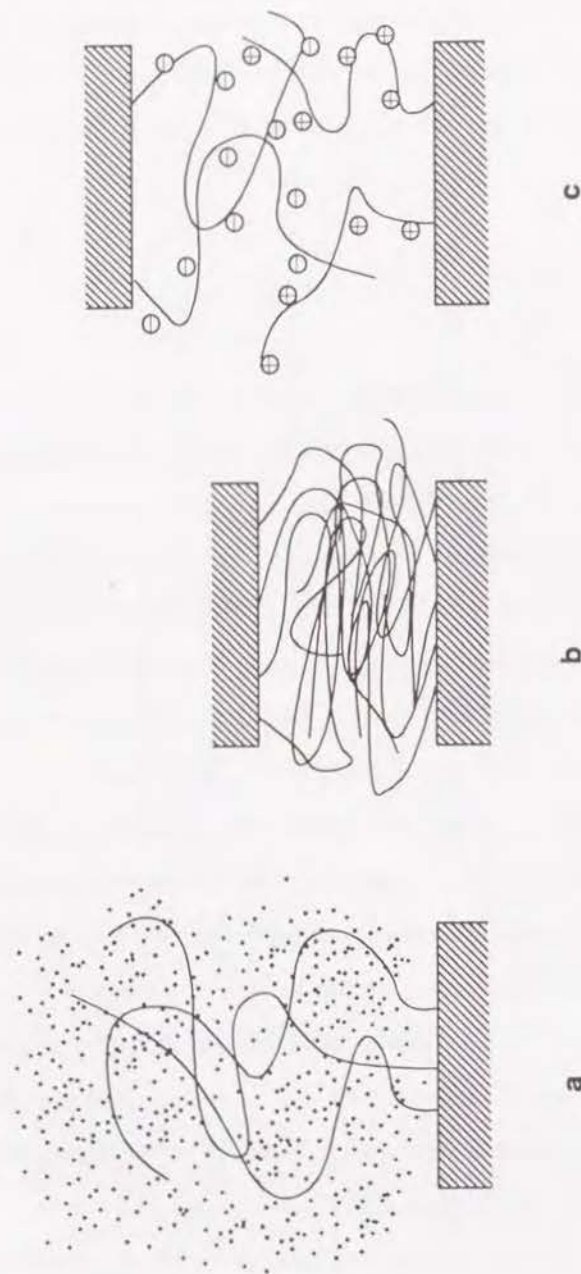


Fig. 9. Schematic representation of water-soluble graft chains on film surface.
 a. diffused graft chain before drying.
 b. mechanically entangled graft chains.
 c. polyion-complexed graft chains with opposite charges.

and then dried, as demonstrated in Figure 4. The result given in Figure 2 indicates that one of the two surfaces should not be necessarily grafted with water-soluble polymers to achieve substantial adhesion, although grafting onto both surfaces leads to stronger adhesion. One exception is the pair having ionic groups of the same sign. As demonstrated in Figure 6, adhesion between two charged surfaces with the same sign was very weak so long as the wet films were not sufficiently dried, especially for the anionic-anionic pair. This is not due to the presence of plenty of water, because adhesion between two oppositely charged surfaces was strong even before drying as shown in Figure 7. In this case it is highly probable that the Coulombic attractive force is operating between the two opposing surfaces, almost independent of the presence of water. The shear strength of the lap between two AAc-grafted surfaces is low for short times but increases to a high value after ca. 70 minutes. The low value could well be the result of a low cohesive strength of the resulting AAc polymer film which is plasticized with water. The time for the increased strength compares well with the drying up time for these thick layers ($190 \mu\text{g}/\text{cm}^2$). An explanation for that might be that the cohesive strength of the adhesive layer increases due to: a) smaller plasticizing effect and b) well known formation of dimers between carboxyl groups. The interaction of groups of amine derivatives (a Brönstedt and a Lewis base) with the carboxyl groups through protonation of the former by the latter is also quite plausible for the enhanced adhesion strength between AAc-grafted(anionic) and DMAPAA-grafted(cationic), in addition to electrostatic interactions. The assumption was further confirmed by the study performed on this anionic-cationic pair in the presence of NaCl which generally suppresses the Coulombic interaction in aqueous medium as a result of increased ionic strength of the medium. As shown in Figure 7, the addition of NaCl to water clearly reduced the adhesion force between the negatively charged and the positively charged surfaces.

The findings obtained in this study is not sufficient to identify the failure mode of adhesion, but it seems probable that the failure mode between a grafted and a non-grafted surface is adhesive because the grafted chains are fixed on the substrate polymer by the chemical bond which is much stronger than the van der Waals one. In the case of the adhesion between two grafted surfaces, the result of repeated measurements of adhesion

shown in Figure 8 seems to suggest that both adhesion and cohesive failures occur.

CONCLUSION

In conclusion, it may be summarized that when a surface-grafted film is contacted with another film in the presence of water, the graft chains function as adhesives, the adhesion force depending on the drying time, hydrophilicity of the adhering surfaces, nature of graft chains, and graft density. The highest shear strength is obtained between two AAm-grafted surfaces. Adhesion between the anionic AAc-grafted and the cationic DMAPAA-grafted surfaces takes place almost instantaneously at a moment of contact, but the adhesion strength second largest, although the electrostatic attractive force was operative in this case.

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PART II

APPLICATION OF LUBRICATING SURFACES

LUBRICATION OF POLYMER SURFACES BY UV-INDUCED GRAFT POLYMERIZATION

INTRODUCTION

Surface modifications of polymer materials have been the objective of a large number of investigations, but little attention has been paid to make a polymer surface frictionless or slippery. Such a frictionless surface is nonetheless important, especially in the field of marine and biomedical technologies. Although there are few widely known man-made materials that have slippery surface, it is not difficult to find slippery surfaces in the biological world. For instance, most of the surfaces of fishes and sea woods are very slippery when contacted with water. There are also many slippery surfaces on tissues and organs in animal bodies. All of these naturally occurring slippery surfaces are extraordinarily hydrophilic, whereas polymers such as cellulose and poly (2-hydroxyethyl methacrylate), although known as hydrophilic, do not become so slippery as the natural organisms when brought into contact with water.

As shown in previous Chapters, surface modifications of polymer were intensively conducted through graft polymerization by the use of various initiation methods including glow discharge, corona discharge, high-energy radiation, UV radiation, and ozone. It has been found that hydrophobic surfaces of polymer become very hydrophilic and often slippery when grafted with water-soluble monomers.

A coefficient of friction (μ value) is commonly used for evaluation of the lubrication of surfaces, but often difficult to determine, especially for elastic and adhesive polymers because of their complicated hysteresis occurring in a cycle of deformation and recovery during the frictional motion, which is probably associated with adhesion force as well as displacement force.

Triolo and Andrade studied frictional properties of various polymers with the aid of a tensile testing machine. They measured the frictional force generated on the polymer surface during traveling on a glass plate in aqueous environments. They divided the frictional profiles into five types; (1) sharp peaks with steep slopes, (2) sharp peaks with rapid fall but slow rise, (3) low and amplitude high-frequency, (4) relatively smooth curve, and (5) smooth but increasing with time.

The purpose of the present chapter is to modify polymer surfaces by graft polymerization for reducing their μ value in a hydrated state to such an extent as becoming slippery. PP, nylon 6, and EVA were employed as substrate polymers, and AAm and DMAA were used as nonionic water-soluble monomers. A UV irradiation technique was chosen for the graft polymerization of the monomers to the surface of the substrate polymers because of its relatively simple procedure.

EXPERIMENTAL

Materials

Films of PP and nylon 6 were of commercial grade with the thickness of approximately 20 μm . Films of EVA were prepared by casting their toluene solution on a glass plate to have thickness of 0.1 mm. The VA contents of the EVA used were 4, 19, 28, and 33 mol %. Purification of the films was performed by Soxhlet extraction for 24 h with acetone for PP and with methanol for nylon 6 and EVA. The AAm and DMAA monomer were purified before use by recrystallization from the aqueous solution and by distillation, respectively.

Graft Polymerization

Unless otherwise noted, graft polymerization was carried out as follows. Following UV irradiation in air at room temperature with a high-pressure mercury lamp (75 W, Toshiba SHL-100 UV type, $\lambda > 254 \text{ nm}$), they were placed in a deaerated 1.4 M aqueous solution of the monomers and kept at 50°C for 1 h to allow graft polymerization to proceed. The grafted films were first washed with running tap water and then immersed in a distilled water at 70°C for 12

h under continuous stirring to remove the homopolymer. The amount of polyacrylamide(PAAm) grafted was determined with the ninhydrin method as described elsewhere[1]. Contact angles (θ) of the films against water were measured at 25°C with a sessile drop method.

To effect graft polymerization without degassing, a preirradiated EVA film was placed in the aerated DMAA solution to which riboflavin was added. Graft polymerization was allowed to proceed under UV irradiation.

Determination of μ Value

The μ value of the fully hydrated surfaces was measured against a cleaned glass plate using the apparatus illustrated in Figure 1. A slider (A), at the bottom of which a sample film (B) was attached, was allowed to horizontally travel on the glass plate (C) in the distilled water (D) under a load (E). The force needed for the slider to travel at a rate of 10 mm min^{-1} was converted by a low-friction pulley (F) to a vertical force, which was continuously recorded using a 100 g load cell(G). As an example, Figure 2 shows the forces required for a slider attached

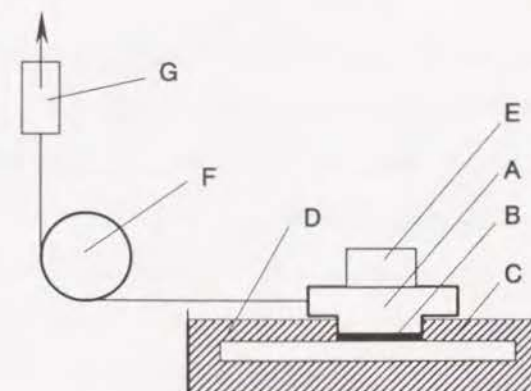


Fig. 1 Schematic of the apparatus used for determining the coefficient of friction, μ , of a hydrated surface against a glass plate in water: (A) slider; (B) sample film; (C) glass plate; (D) distilled water; (E) load; (F) pulley; (G) 100 g load cell.

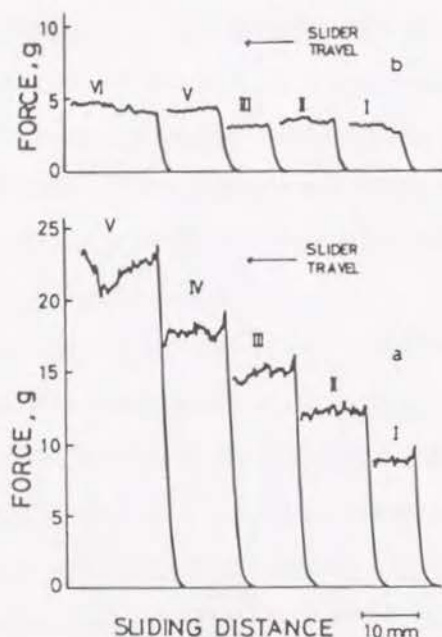


Fig. 2. The force required for a slider attached with the starting PP film (a) and the PAAm-grafted PP film (b) to travel on the glass plate in water. Loads on the slider: (I) 0 g; (II) 10 g; (III) 20 g; (IV) 30 g; (V) 50 g; (VI) 100 g.

to the films before and after graft polymerization to travel under different loads. As is seen, the force-sliding distance curves for the nongrafted PP film have a high peak at the initial stage of transition from the static state to the dynamic motion and then exhibit many spikes during traveling on the glass plate, whereas the curves for the grafted PP film are very smooth and lack the initial high peak. Appearance of many peaks for the nongrafted film may be due to adhesion or mechanical interlocking between the slider and the film surface. This tendency must become more remarkable as the elasticity of the sample polymer increases.

The average force during sliding and the maximum static force at the initial motion are plotted against the load put on the slider in Figure 3. A small difference between the static and the dynamic friction for the starting PP film suggests that the elastic deformation seems to have little effect on the frictional property of the PP film. The slope of the plots gives the μ value.

In the following, only the coefficient of dynamic friction will be given, because the difference in μ between the static and the dynamic friction is in every case insignificant. When the plots in Figure 3 is extrapolated to the negative loads, all the straight lines cross at a single point(A). The frictional force(F_A) at A is probably due to the friction caused by the rotation of the pulley and additional frictions other than that of the tested interface itself.

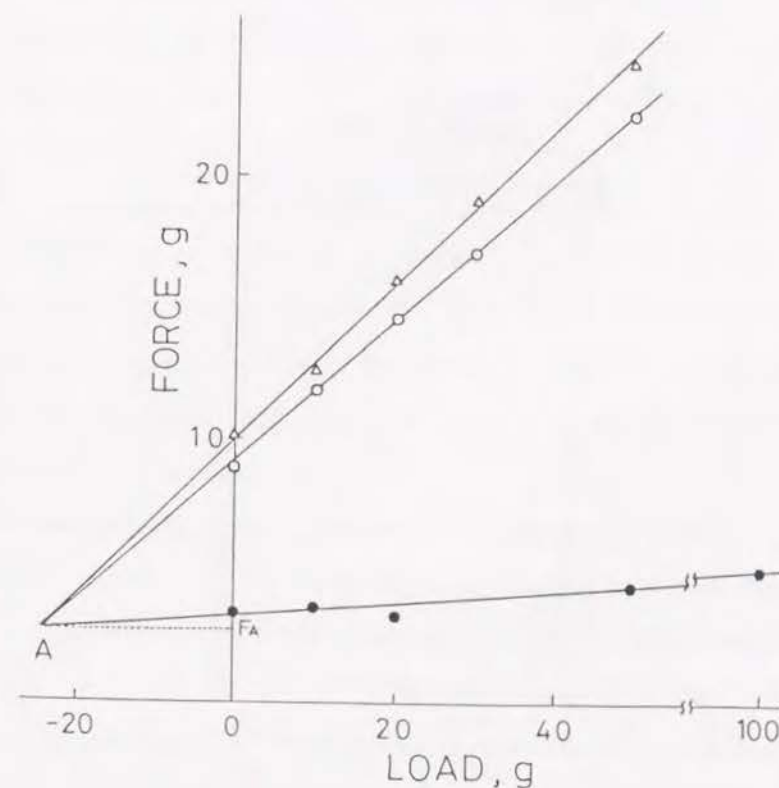


Fig. 3. Plots of the average frictional force against the load put on the slider for the starting PP film (○) and the PAAm-grafted PP film (●). The symbol (Δ) shows the static friction for starting PP film.

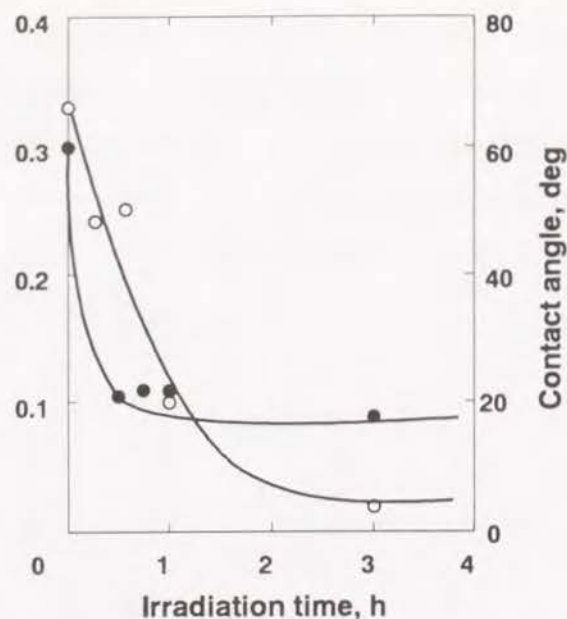


Fig. 4. μ and contact angle (θ) values as a function of UV irradiation time for the acrylamide-grafted nylon 6 films (○) μ ; (●) θ .

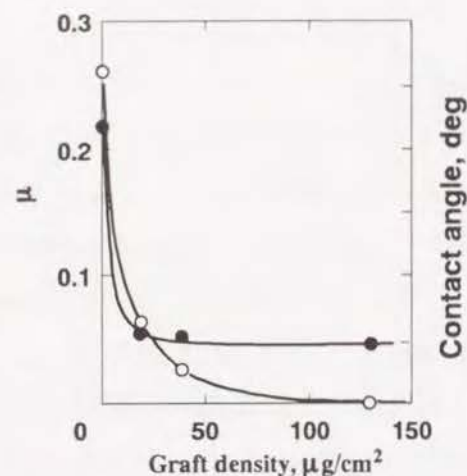


Fig. 5 μ value as a function of graft density for acrylamide-grafted polypropylene films. (○) μ ; (●) contact angle.

RESULTS

PP and Nylon Films

The observed μ and θ values for the PAAm-grafted PP films are plotted against the amount of PAAm grafted in Figure 4. It is seen that both the μ and θ values are remarkably reduced with the increasing graft amount, μ reaching virtually zero when the graft amount becomes larger than $100 \mu\text{g}/\text{cm}^2$. The PP films grafted to such a high amount were felt very slippery when touched with wet fingers. Reduction in μ was not observed for any grafted films when the friction measurement was performed in the absence of water.

Figure 5 shows the μ and θ values observed for the PAAm-grafted nylon films. In this case the plots are given against the UV preirradiation time, because the amount of the PAAm grafted onto nylon could not be determined with the ninhydrin method since amide bonds in nylon interfered with those of PAAm in the quantitative analysis. As can be seen from Figure 5, the μ value strongly decreases, similar to the PAAm-grafted PP. This is a good evidence for occurrence of graft polymerization of AAm onto the surface of UV-preirradiated nylon films. Straightforward comparison of Figure 5 with Figure 4 reveals that UV preirradiation for 3 h onto the nylon film, followed by graft polymerization of AAm, might yield a graft amount ranging between 50 and $100 \mu\text{g}/\text{cm}^2$.

PP and nylon films treated with UV irradiation alone did not exhibit any significant reduction in μ and θ . The results are shown in Figure 6, which indicates that the μ value practically is not altered upon UV irradiation both for the PP and the nylon film, although θ is somewhat reduced for the nylon film. The different change of the contact angle for the PP and the nylon film may be ascribed to different yields of hydrophilic groups on the films upon UV irradiation. As is obvious from Figures 4 and 5, graft polymerization of water-soluble monomers onto the UV-irradiated films reduced their contact angles in addition to the μ values.

EVA films

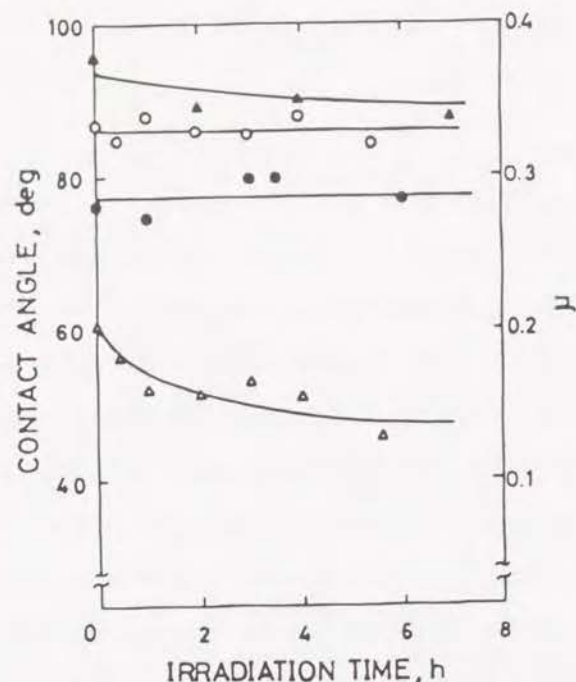


Fig. 6. Influence of UV irradiation alone on the contact angle (open symbols) and the μ value (filled symbols) of PP and nylon 6 films: (O, ●) PP; (Δ , $\blacktriangle$) nylon 6.

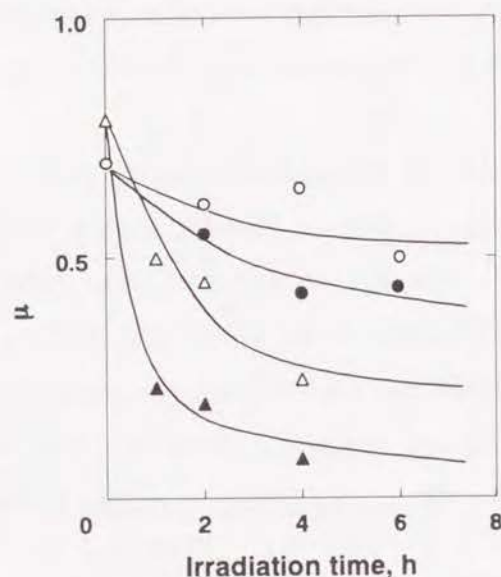


Fig. 7. Influence of UV preirradiation time on the μ value of surface-grafted EVA films with different VA contents: (O, ●) VA 14 mol %; (Δ , $\blacktriangle$) VA 28 mol %; (O, Δ) poly(acrylamide)-grafted; (●, $\blacktriangle$) poly(dimethylacrylamide)-grafted.

Following UV preirradiation, EVA films with different VA contents were subjected to graft polymerization of AAM and DMAA monomer. The condition for graft polymerization was the same as for the PP and nylon films. The μ value of the grafted EVA films is given as a function of the UV preirradiation time in Figure 7. Clearly, the μ value decreases with time of UV irradiation and it takes longer irradiation time for the EVA film of lower VA contents to have a lubricating surface. It is also seen that the PDMAA-grafted films become more slippery than the PAAm-grafted if irradiation is performed for the same period of time.

The higher μ values of the grafted EVA films of 14 mol% VA is due undoubtedly to the lower potential of the EVA film for the graft polymerization than that of the film of 28 mol% VA. However, the lower μ value of the DMAA-grafted EVA film than that of the PAAm-grafted does not mean that PDMAA should be more capable of producing a slippery surface than PAAm, because the amount of the grafted chains might be different between PAAm and PDMAA, even though the films are irradiated with UV for the same duration. However, as is shown in Figure 8, the μ value of the EVA films is practically not dependent on the VA content, if the μ value is compared at the same graft amount. If it is close to zero, the μ value may be still governed by the surface property of the starting EVA substrates which is dependent on the VA content.

Figure 9 shows the effects of duration and temperature of graft polymerization of DMAA on the μ value of the grafted EVA film. In this case the EVA films of 33 mol% VA was preirradiated at room temperature for 30 min with a low-pressure mercury lamp (32 W, Riko-32L type), followed by graft polymerization at different temperatures under UV irradiation in the presence of riboflavin without degassing. Riboflavin was employed because it consumed the oxygen present in the monomer aqueous solution upon UV irradiation (see Chapter III). Otherwise, the oxygen would inhibit the graft polymerization. As can be seen from Figure 9, raising the polymerization temperature had a large effect on reduction of the μ value of the grafted EVA surface. For instance, a highly slippery surface could be achieved without deterioration of the bulk property in a short period of time such as 30 min both for preirradiation

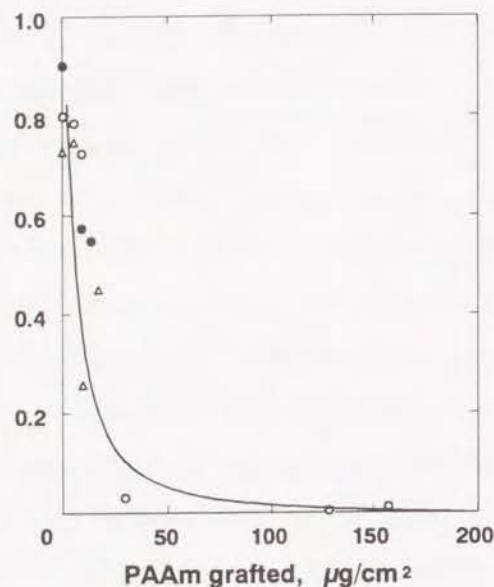


Fig. 8. μ values as a function of the graft density for acrylamide (AAM)-grafted ethylene-vinyl alcohol copolymer films:
(O) VA 28 mol %; (●) VA 19 mol %; (Δ) VA 14 mol %.

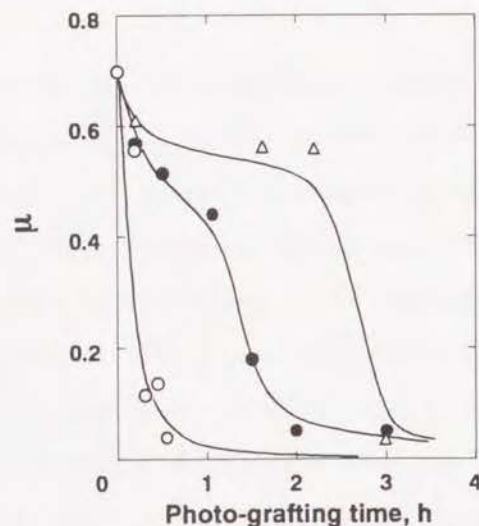


Fig. 9. Effect of photografting time on the μ value of the ethylene-vinyl acetate copolymer films with VA content of 33 mol % at various temperatures $^{\circ}$ C): (O) 65; (●) 30; (Δ) 10.

and graft polymerization when the preirradiated film was subjected to polymerization at 65 $^{\circ}$ C.

In an attempt to prepare a catheter which has a slippery surface when hydrated, a tube with a diameter of 5 mm was fabricated by extrusion of the EVA pellet used for the film. The surface of the tube became slippery almost to an extent similar to the film when grafted with DMAA under the same condition as for the film. No significant difference in the observed μ value was found between the tube and the film. Detailed results for catheter tube will be described in the next Chapter.

Table I Contact angles (θ) and coefficient of frictions (μ) of various polymer films before graft polymerization.

	PP	Nylon	EVA (VA content)				PTFE ^a
			14 %	19 %	28 %	33 %	
θ	89	59	83	80	79	74	119
μ	0.27	0.38	0.68	0.90	0.80	0.68	0.09

^aPolytetrafluoroethylene.

DISCUSSION

Lubrication of a polymeric material in the presence of water appears to be closely related to hydrophilicity(or hydrophobicity) of the surface. Fluorinated polymers are known to have the lowest friction coefficient in air among the conventional polymers, but do not become slippery when hydrated. The substrate polymers employed in the present work are PP, nylon, and EVA with different VA contents. The unmodified surfaces of these films have different contact angles against water and μ values, as given in Table I, where those of polytetrafluoroethylene(PTFE) are also given for comparison. Their μ value before graft polymerization is plotted against their

water contact angle in Figure 10. As is seen, the μ value of these ungrafted surfaces determined against a glass plate in an aqueous environment varies in a peculiar manner with the increasing contact angle. A maximum is observed for the μ value at a contact angle around 80° . In Figure 10, the average values for the surfaces grafted with AAm or DMAA are also plotted, the contact angle(θ) and the μ value being 20 and 0.01, respectively.

Appearance of a maximum in the θ - μ relation reminds us of the work of adhesion of a reference material to polymer surfaces of various θ s in water. The result is rewritten in Figure 11. The work of adhesion in water, $W_{12,w}$ was theoretically derived as a function of the interfacial free energy between a polymer surface and water, γ_{1w} [9]. One of the most proper quantity identifying hydrophilicity (or hydrophobicity) of a surface is the γ_{1w} value. As seen from Figure 11, $W_{12,w}$ increases with the increasing γ_{1w} or hydrophobicity, but, after passing a maximum, decreases as γ_{1w} becomes much higher. This result implies that a quite hydrophobic surface interacts very weakly with the opposing surface to an insignificant extent if water is present. This seems reasonable because a water thin layer must be bound to the highly hydrophilic surface, leading to very weak adhesion between the waterlike surface and the reference in the presence of water.

Similar to adhesion, friction must be directly concerned with the attractive force between the two opposing surfaces in contact, if both of them have entirely smooth and undeformable surface. Strong friction may take place if a strong attractive force is operative between the opposing surfaces, whereas friction may be insignificant if the attractive force is weak. In the present work, friction was determined in the presence of water using a glass plate as the reference. It is likely that a more hydrophobic surface has less attraction to the glass plate, resulting in smaller friction. On the other hand, a more hydrated surface with a larger amount of water-soluble graft chains will also interact less strongly with the glass plate, as mentioned above. We can directly feel the surface slippery upon touching it with fingers, if the μ value between the surface and our finger is below a certain value.

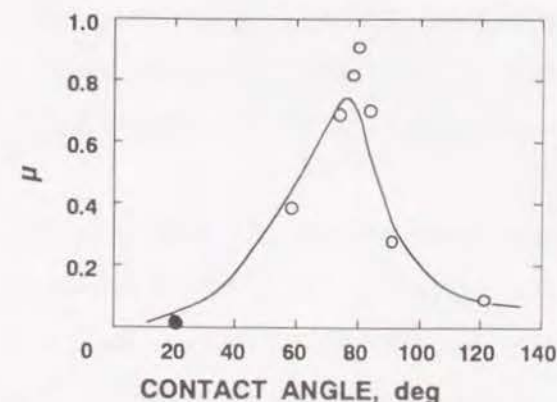


Fig. 10. Relation between the coefficient of friction μ and the water contact angle of films. (O) ungrafted; (●) grafted.

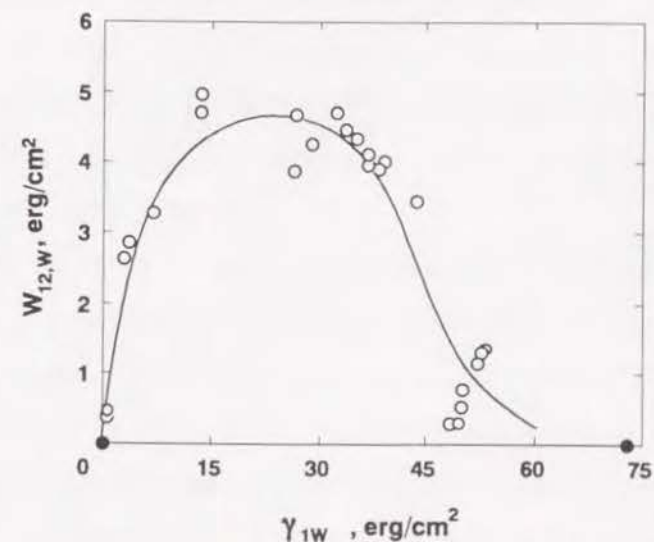


Fig. 11. Work of adhesion of polymer surface 1 with a reference surface 2 in water ($W_{12,w}$) as a function of the interfacial free energy between water and the polymer surface 1 (γ_{1w}).

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Chapter VII

LOW-FRICTIONAL CATHETER MATERIALS BY UV-INDUCED GRAFT POLYMERIZATION

INTRODUCTION

Polymeric materials with a slippery or low-frictional surface have wide applications in biomedical technologies[1]. For instance, low-frictional surface would enable smooth insertion of urinary, tracheal, and cardiovascular catheters without injury to the mucous membranes of inserted organs and without giving intolerable pain to patients. It is also likely that endoscopes could be more readily inserted into intestines if they had a slippery surface.

Currently, smooth catheterization and insertion are achieved by applying lubricants or jelly-like materials or coating a hydrogel onto the catheter surface. Lidocaine jelly is commonly used because of its additional local anaesthetic effect. However, these agents applied on catheters are not effective after a long period of time, due to their elution into the adjacent body liquid. The hydrogel coating does not give a highly slippery surface for long, compared with the surface grafting of water-soluble polymers[2].

Surface modifications of polymeric materials through graft polymerization with glow discharge[3], corona discharge[4], high-energy[5] and UV radiations[6], and ozone[7] were already studied. The hydrophobic surfaces were found to become almost permanently very hydrophilic and slippery when grafted with water-soluble monomers and then hydrated. The purpose of the work in this chapter was to prepare catheter materials possessing a low frictional surface. EVA and plasticized PVC were chosen as the substrates and DMAA as the monomer. The LD₅₀ of DMAA is almost twice of that of acrylamide[8]. UV preirradiation and subsequent photopolymerization in the presence of riboflavin was employed for the surface graft

polymerization, since this eliminates the tedious degassing procedure that limits large-scale production. The lubricity of films and tubes of EVA and PVC is evaluated from their coefficient of friction and friction drag.

EXPERIMENTAL

Materials

The content of vinyl acetate of EVA is 28 and 33 mol%. Unless otherwise noted, EVA with the vinyl acetate content of 28 mol% is used throughout this work. EVA film was prepared by casting the 5 wt% toluene solution on a glass plate to a thickness around 0.1 mm. Purification of the film was performed by Soxhlet extraction with methanol for 24 h. The PVC used for tubing was plasticized with di-(2-ethylhexyl) phthalate (concentration of plasticizer is 30 wt%). Catheter-like tubes of EVA (outer diameter 4.1 mm and wall thickness 0.75 mm) and PVC (outer diameter 4.0 mm and wall thickness 0.75 mm) were fabricated by extrusion without using any releasing agents followed by thermal sealing of one end of the tubes. The DMAA monomer was purified by conventional distillation just before use. Riboflavin of analytical grade was used as received.

UV Irradiation and Graft Polymerization

Unless otherwise noted, UV preirradiation and graft polymerization were carried out according to the method described in Chapter III[9]. Briefly, the dried polymeric substrates were irradiated with UV from a low-pressure mercury lamp (32 W, Riko-32 L type) in air at room temperature by placing them about 7 cm away from the center of the light source. After that, they were immersed in the aqueous monomer solution containing a small amount of riboflavin, the concentration of DMAA and riboflavin being kept mostly at 1.0 M and 10–5 M, respectively. The mixture was kept at 60 °C and irradiated by a high-pressure mercury lamp (400 W, Riko-400 HL type) at a distance of 10 cm for a given period of time to effect graft

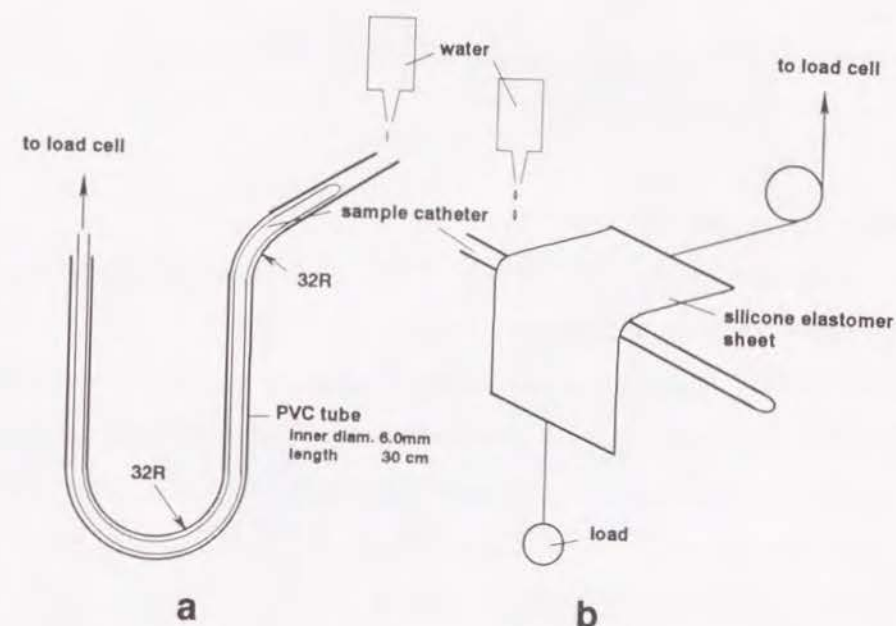


Fig. 1. The methods for determining the frictional force of catheter materials under wet conditions against a plasticized PVC tube (a) and a silicone elastomer sheet (b).

polymerization. For both the irradiations, care was taken for the films, the tubes, and the monomer solutions with the immersed substrates to be homogeneously irradiated by the UV lights. To remove the homopolymer formed, the grafted polymeric materials were first washed with running tap water and then immersed in distilled water at 70 °C for 20 h under continuous stirring using an ultrasonicator. Although poly(acrylamide) could be successfully determined quantitatively by the ninhydrin method, we could not find any analytical means to determine the amount of polyDMAA with high accuracy, when the amount was small. However, gravimetry

could be applied to the EVA tube when it had large surface areas.

Optical Microscopy

The cross-section of the grafted tubes was observed by light microscope at magnification of x40 after staining with rhodamine B.

Measurement of Surface Lubricity

The coefficient of friction (μ) of the fully hydrated EVA films was determined against a cleaned glass plate, according to the method described elsewhere[9].

The lubricity of the hydrated surfaces of grafted catheter-like tubes was evaluated by measuring the maximum force to pull out the tubes from a plasticized PVC tube with an inner diameter of 6.0 mm or to slide a silicone elastomer sheet against the grafted tubes. For both cases, the friction drag forces were measured by a load cell under wet conditions. The devices employed for the measurements are depicted in Figure 1.

RESULTS AND DISCUSSION

In Chaptre II, it was represented that UV irradiation of polymers in the presence of air can generate polymeric peroxides, which are capable of initiating polymerization of monomers upon thermal decomposition to free radicals unless oxygen is present in the monomer solution[9]. In addition, it has been found that the oxygen existing in the monomer solution can be eliminated without any degassing procedure but simply by UV irradiation of the monomer solution if a small amount of riboflavin is present in the solution. Riboflavin consumes the dissolved oxygen upon UV irradiation[10]. Therefore, throughout the present study, degassing from the monomer solution was not conducted, but 10^{-5} M riboflavin was added to the monomer solution and UV irradiated. For comparison, graft polymerization was carried out after degassing the monomer solution but without UV irradiation.

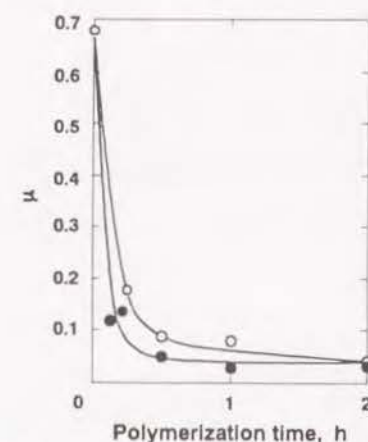


Fig. 2. The coefficient of friction μ as a function of polymerization time for ethylene-vinyl acetate copolymer films surface-grafted with N,N-dimethylacrylamide after UV preirradiation for 30 min with a low-pressure mercury lamp. O, thermal polymerization at 65°C under de-aerated conditions; ●, photopolymerization at 65°C in the presence of riboflavin without degassing.

EVA films

EVA provides a good thermoplastic elastomer without using any additives such as plasticizer and, hence, is employed currently for blood bag and drug delivery system carrier in the medical field. The EVA films were UV irradiated in air with a low-pressure mercury lamp for 30 min. Half of the preirradiated films were graft polymerized without degassing but under UV irradiation. For comparison, the other half were placed in a deaerated monomer solution and heated to 65 °C to effect graft polymerization. The observed μ values for the grafted films are plotted against the polymerization time in Figure 2. As can be seen, the μ values are drastically reduced from 0.7 to less than 0.1, indicating that graft polymerization effectively took place within 0.5 to 1 h, irrespective of the deaeration method. As the difference in μ of the grafted films between the de-aerated and aerated (riboflavin) graft polymerization methods was not significant (Figure 2), the following graft polymerization was carried out without degassing, but in the presence of riboflavin because of its more simple procedure.

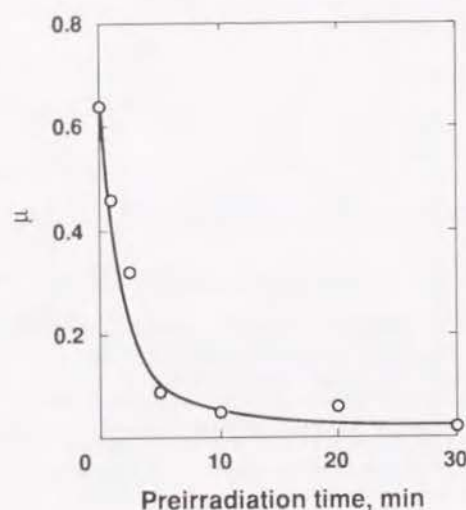


Fig. 3. The coefficient of friction as a function of UV preirradiation time for ethylene-vinyl acetate copolymer films surface-grafted with N,N-dimethylacrylamide.

As the μ value must be greatly affected by the extent of graft polymerization, the effects of variables of graft polymerization on the μ value were studied in more detail.

The effect of UV preirradiation time on the μ value of grafted films is given in Figure 3. Graft polymerization of DMAA onto the preirradiated films under UV irradiation was carried out at 30°C for 2 h. Figure 3 shows that preirradiation for 5–10 min was sufficient to produce a slippery surface. When touched with fingers, the hydrated surfaces of $\mu < 0.1$ felt very slippery. It is possible that EVA may suffer photodegradation if irradiation is prolonged, but, in the present case, UV irradiation for 30 min had little effect on both tensile strength and elongation at break of the films (Table 1).

The effect of the monomer concentration on the μ value of the grafted films is given in

Figure 4. EVA films were preirradiated with UV for 30 min and then immersed in aqueous monomer solution of various concentrations of DMAA kept at 60 °C. The solution was subjected to UV irradiation for 1 h to effect graft polymerization. Figure 4 shows that 0.25 mol l⁻¹ of DMAA monomer solution is enough to reduce the μ value below 0.1.

Table I Effect of UV irradiation on the mechanical properties of ethylene-vinyl acetate (EVA) copolymer films.

EVA film	Tensile strength, kg/cm ²		Elongation at break, %	
	min.	max.	min.	max.
Virgin	175	205	1009	1227
UV irradiated for 30 min	169	218	1013	1136
UV irradiated for 1 h	172	227	1000	1190
Surface-grafted	188	206	1001	1090

EVA tubes

The EVA tubes were surface-grafted in the same manner as the EVA films, except for the following two points. Firstly, the tubes had to be rotated around themselves during both UV preirradiation and graft polymerization under UV irradiation for the surfaces to be homogeneously irradiated. With real irradiation time T_r , the effective dose time per unit area of the tube surface (T_e) is given by:

$$T_e = 1/\pi T_r \quad (1)$$

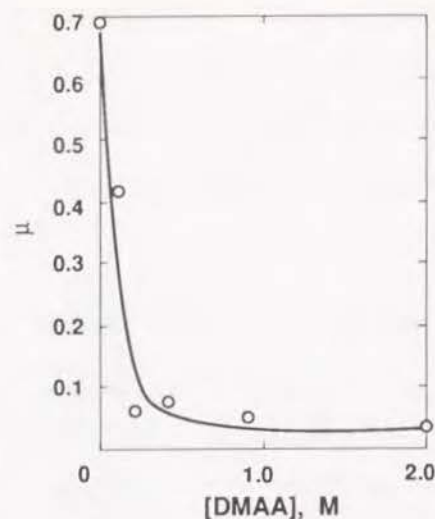


Fig. 4. The coefficient of friction as a function of N,N-dimethylacrylamide (DMAA) monomer concentration for ethylene-vinyl acetate copolymer films surface-grafted with DMAA after UV preirradiation for 30 min with a low-pressure mercury lamp.

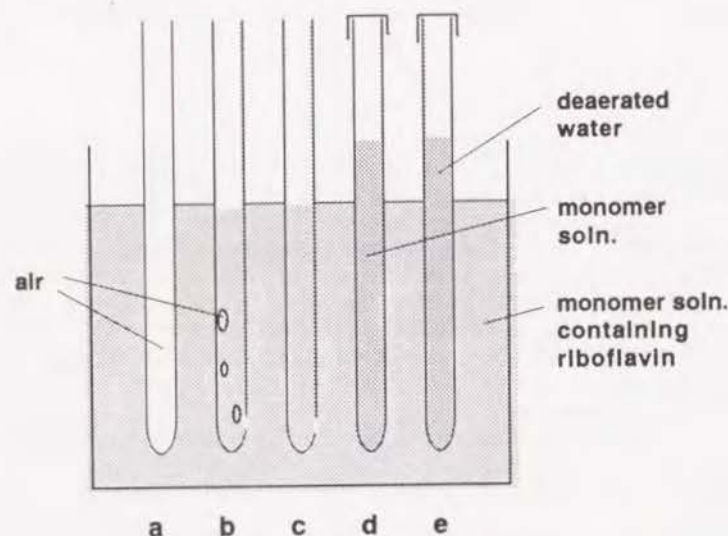


Fig. 5. Various methods employed for graft polymerization on to an ethylene-vinyl acetate copolymer tube in the presence of riboflavin. (a) Tube with closed end immersed in monomer solution with air inside the tube. (b) Tube with 4 mm diam. hole automatically filled with monomer solution. (c) Air bubbles removed from the monomer solution in the tube by syringe before UV irradiation. (d and e) Tubes with monomer solution and pure water respectively.

irrespective of the angular velocity, provided that the tube is rotating at a constant rate. This equation can be derived by taking into account the rotation of the tube. The increment of light intensity received by the unit area of the rotating tube surface is reduced by a factor of $I_0 \cos \theta d\theta$, when the normal light intensity is I_0 and the incident angle increases from θ to $\theta + d\theta$. The total intensity which the unit area receives in one rotation is $2I_0 (= \int_0^{2\pi} I_0 \cos \theta d\theta)$, since θ changes from 0 to π in one rotation (no light from π to 2π). On the other hand, the perpendicularly facing, non-rotating surfaces receive $2\pi I_0$ in the same time. Therefore, the rotating tube surface receives less light than the non-rotating one by a factor of π . In the following, the irradiation time will be given by T_r .

The second point is that it was always necessary to remove air bubbles generated inside the tubes, as the excessive oxygen present in the monomer solution prevents graft polymerization almost completely. Therefore, the tubes to be brought into contact with the monomer solution were processed in various ways, as illustrated in Figure 5. In (a), the tube with the closed end is simply immersed in the monomer solution and the inside of tubes is occupied by air. The tube in (b) has a hole of 4 mm diameter at the lower site so as to be automatically filled with the monomer solution. In this case air bubbles are generally formed at the inner wall of tube. In (c), all the air bubbles are carefully removed from the monomer solution in the tube by syringe before UV irradiation. The tubes of (d) and (e) have no hole, but are simply filled with the monomer solution and pure water from the outside, respectively.

When the outer surface of UV-preirradiated tube was brought into contact with the monomer solution in these different ways and irradiated with UV, the tubes of (c), (d), and (e) allowed effective grafting with DMAA, whereas (b) gave partially grafting and (a) not at all. This indicates that the air in the tube strongly inhibits graft polymerization. The extent of graft polymerization was not significantly different among (c), (d) and (e).

The distribution of the graft chains in the substrate was studied by staining the cross-section of grafted EVA tube (Figure 6). Graft polymerization of DMAA was localized in the outer surface of the tube wall, probably because the monomer could not virtually penetrate into the

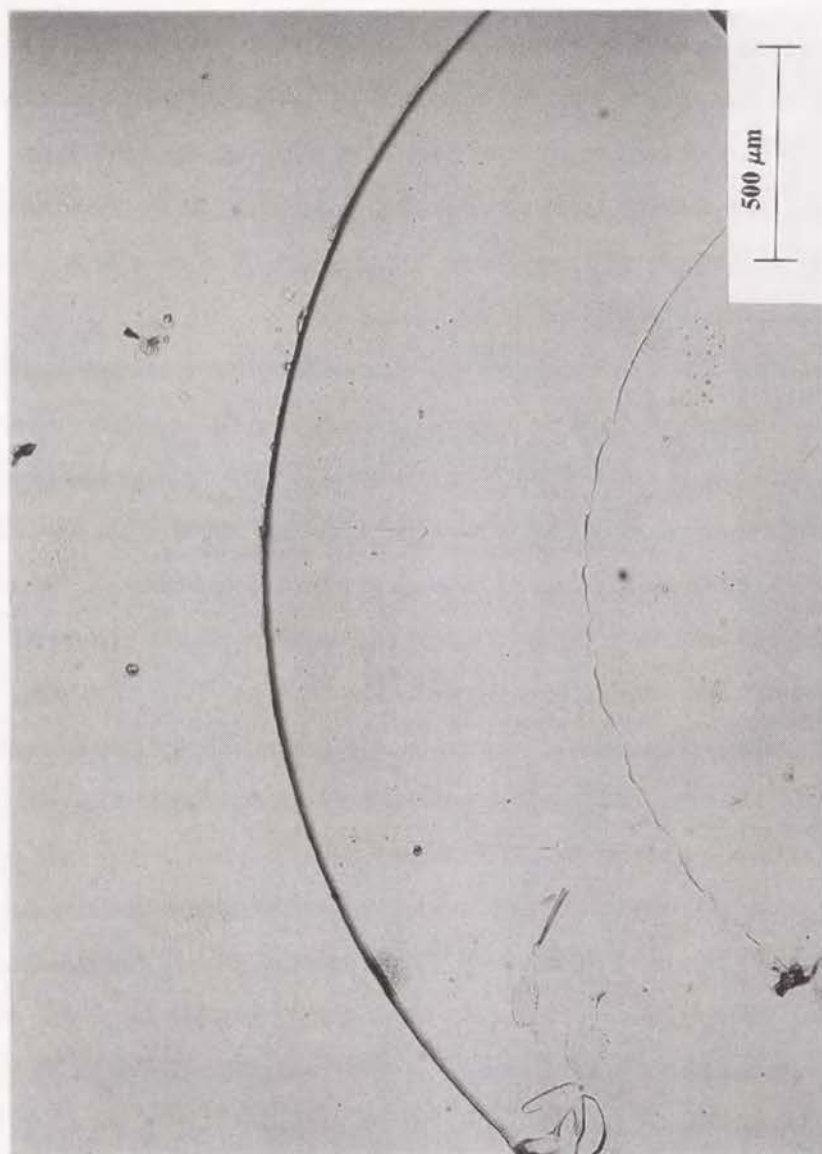


Fig. 6. Optical micrograph of the cross-section of ethylene-vinyl acetate copolymer tube grafted with *N,N*-dimethylacrylamide and subsequently stained with rhodamin B.

polymer interior from the outside.

To evaluate the lubricity of the grafted tube, the virgin EVA tube without a hole was first UV irradiated for 30 min, filled with pure water, and then degassed. The tube with the degassed water was subjected to surface graft polymerization of DMAA, according to the method (c) in Figure 5. The graft tube was inserted in a PVC tube having a larger diameter and the interstice was filled with water (Figure 1a). The force required to pull the grafted EVA tube from the outer PVC tube is listed in Table II, together with the polymerization conditions. EVA with vinyl acetate contents of 28 and 33 mol% were used and the amount of polyDMAA grafted was determined by gravimetry. As a tube of length 35 cm was used, gravimetry could be carried out when the graft amount was large. The detection limit was about $60 \mu\text{g cm}^{-2}$.

Table II The force required for the ethylene-vinyl acetate copolymer tubes surface-grafted with *N,N*-dimethylacrylamide (DMAA) to pull out from the covering plasticized poly(vinyl chloride) tube.

Vinyl acetate content, mol %	Monomer conc., M	Polymerization time, min	DMAA grafted, $\mu\text{g/cm}^2$	Pulling force, N
28	1.0	15	ND*	0.321
	1.0	30	120	0.325
	2.0	30	264	0.128
	3.0	15	ND*	0.216
33	1.0	30	243	0.185
	2.0	30	450	0.068

* Not detectable when determined by gravimetry.

Table II shows that higher the monomer concentration and the longer the polymerization time, the more grafted polyDMAA was obtained. As described in Chapter III, higher vinyl acetate content in EVA led to more marked graft polymerization. The pulling forces listed in Table 2 range from 0.068 to 0.325 N, almost in parallel with the grafted amount of polyDMAA.

As the pulling force is as large as 20 N for the ungrafted EVA tube, one can say that the observed force less than 0.3 N is extremely small. Indeed, all the surfaces of these grafted tubes were very slippery when hydrated. Estimation of the frictional coefficient from the pulling force was not possible because the measuring system had so complicated structure.

PVC Tubes

The PVC plasticized with di-(2-ethylhexyl) phthalate, a raw material for widely used disposable urinary catheters, was also surface-grafted with DMAA by the above method. To study the frictional property of the surface-grafted PVC surface, a PVC tube was UV-preirradiated for 30 min and graft polymerized with DMAA at 60 °C for 30 min according to the method (e) in Figure 5. The maximal frictional force needed for a silicone elastomer sheet to slide on the wet PVC tube was repeatedly determined with the method shown in Figure 1b.

The observed frictional forces for the grafted PVC tube are plotted against the number of measurements in Figure 7, together with those for the ungrafted, uncoated PVC tube. Figure 7 shows a frictional force of approximately 10 N for the ungrafted PVC tube, but about 2 N or less for the PVC tube grafted with DMAA and the tube coated with jelly, at least at the first measurement of the frictional force. Although the surface-grafted PVC maintained the frictional force to less than 0.5 N even at the 50th measurement, the PVC tube merely coated with lidocaine jelly lost gradually its surface lubricity with the increasing number of rubbings against the silicone sheet. The frictional force was 0.7 N for the DMAA-grafted PVC tube which was immersed in boiling water for 5 h under strong ultrasonic vibration to remove homopolymer, while the frictional force was 0.5 N for the PVC tube extracted with water at 75 °C for 20 h to remove the homopolymer. This strongly suggests that the polyDMAA chains are grafted to the PVC and stable against mechanical rubbing, similar to the poly DMAA chains grafted to EVA.

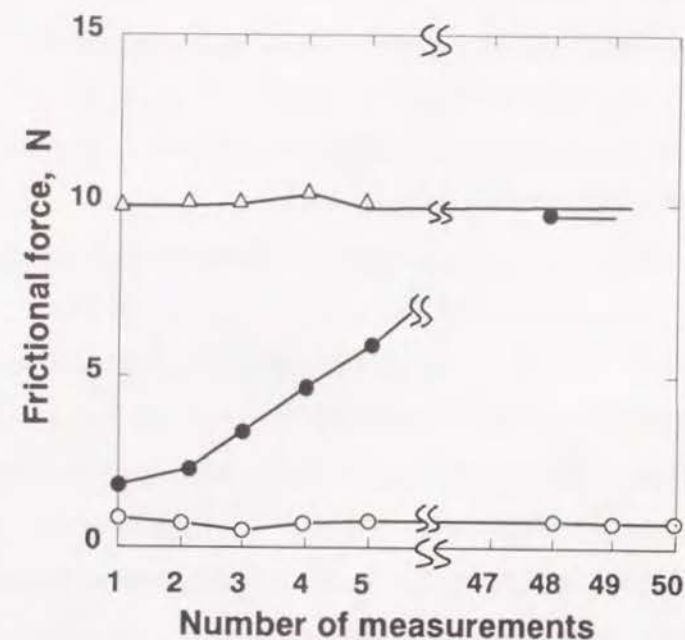


Fig. 7. Influence of the number of measurements on the frictional force required for a silicone elastomer sheet to slide on differently treated poly(vinyl chloride) tube: Δ , untreated; $\bullet$, coated with lidocaine jelly; $\circ$, surface-grafted with N,N-dimethylacrylamide.

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Chapter VIII

SCANNING ELECTRON MICROSCOPE OBSERVATION OF LUBRICIOUS POLYMER SURFACE FOR MEDICAL USE

INTRODUCTION

When biomaterials are to be used for catheterization in urinary, tracheal, and cardiovascular tract, or for endoscopy, their dried surface should be provided with good handling characteristics and is further desired to become slippery upon contact with aqueous body liquid to prevent mechanical injury to mucous membranes and lessen pain of patients[1]. For this purpose, lubricants and jelly-like materials have been applied onto the biomaterials, but cannot maintain a highly slippery surface for sufficiently long duration of time. Therefore, a variety of techniques have been attempted for rendering the polymer surface frictionless for long-term use. Detailed discussion on this subject was given by Fan, who classified hydrophilic lubricious surfaces into five categories[2]. The techniques employed for the lubricious surface preparation include hydrophilic polymer blending[3,4], hydrogel coating[5,6], immobilization of hydrophilic polymeric chains onto the substrate surface[7], and surface graft polymerization of water-soluble monomers[8].

Surface modifications of polymeric materials have been studied through graft polymerization after oxidation with various methods, such as glow discharge[9], corona discharge[10], high-energy radiation[11], UV radiation[12], and ozone[13]. The oxidation of polymer surface produces a sufficiently high concentration of polymer peroxides, which are capable of initiating graft polymerization of monomers upon decomposition. It has been found that a hydrophobic substrate becomes very hydrophilic and slippery almost permanently when surface-grafted with water-soluble polymers and then hydrated. The coefficient of friction, the contact angle, and the friction drag were determined to characterize the lubricated surfaces[14,15].

The total frictional force between two polymeric surfaces is complicated due to surface roughness, mechanical integrity of boundary layer, viscoelastic energy dissipation, van der Waals interaction, and electrostatic and polar interactions between the surface molecules. In Chapter VI[15], the correlation between the friction and the contact angle of surfaces was studied to find that a very hydrophobic surface interacts only weakly with the opposing surface, regardless of the presence of water, whereas a quite hydrophilic surface practically cannot attract the opposing surface if water is present.

In the course of studies on the lubricious surfaces modified by graft polymerization, we accidentally found that the surface structure observed by scanning electron microscopy(SEM) depended on the process of sample preparation for SEM. For instance, a peculiar textured structure was observed when the hydrated, grafted surface was subjected to freeze-drying for SEM sample preparation. This Chapter represents the result, focusing on the surface morphology observed by SEM.

EXPERIMENTAL

Materials

Polyurethane film of 0.1 mm thickness was prepared by casting 5 wt% tetrahydrofuran solution of a commercial polyetherurethane(Pellethane®) on a cleaned glass plate. PET film used for comparison was of commercial grade having thickness around 50 μm . The films were purified by Soxhlet extraction with methanol for 24 h. AAm and DMAA monomers to be used for graft polymerization were purified by recrystallization and distillation, respectively, before use.

Graft Polymerization

Graft polymerization was performed with an ozone method[13]. Briefly, ozone was generated from oxygen by an ozonizer(O-1-2 type, Nippon Ozone Inc., Tokyo) at an ozone concentration of approximately 0.2 vol% in oxygen. Following ozone exposure for 1 min, the polyurethane film was placed in the aqueous solution of monomer in the presence of 10^{-2}

M Mohr's salt and kept at 35°C for 1 h, after degassing to effect redox graft polymerization. The grafted films with different graft densities were prepared by varying the monomer concentration from 0.4 to 2.8 M. Grafting onto the PET film was carried out with the photo-induced polymerization as described in Chapter III[16], since surface graft polymerization onto the PET film was difficult with the ozone method. The grafted films were washed with running tap water and then immersed in distilled water at 70°C for 12 h under continuous stirring to remove the homopolymer as thoroughly as possible. Although the AAm polymer could be successfully determined quantitatively by the ninhydrin method[9], we could not find any effective analytical means to determine the DMAA polymer with high accuracy. However, gravimetry could be applied to the films, when the surface area was larger than 5 x 5 cm^2 and the weight of polyurethane was about 0.3 g. The detection limit was about 20 $\mu\text{g cm}^{-2}$.

Surface Analysis

X-ray photoelectron spectroscopy(XPS) and Fourier-transform infrared spectroscopy coupled with attenuated total reflection (ATR FT-IR) of the surface-grafted films were measured with ESCA750 and FTIR-8100 manufactured by Shimadzu Inc., Kyoto, Japan, respectively. For the ATR FT-IR measurement, the film sample was placed on the ATR crystal(KRS-5) under pressure. The C_{1s} peak for hydrocarbon(285.0 eV) was chosen for the standardization of the XPS evaluation. The coefficient of friction(μ) of film surface was measured against a cleaned glass plate in water using an apparatus described in Chapter VI[15]. Briefly, a slider of 1.0 x 1.5 cm^2 , at the bottom of which the film was attached, was allowed to horizontally travel on the glass plate in distilled water. The μ value was calculated from the slope of the plot of the average force during traveling at a rate of 10 mm min^{-1} against the load on the slider.

Surface Observation

Optical photographs were taken after staining the cross-section of grafted surface with Skyblue 6B, which was not able to stain the hydrophobic substrate polymer but only the

grafted hydrophilic region. SEM observation of the grafted surface was performed using a scanning electron microscope (S-450 type Hitachi, Tokyo, Japan) at magnification from 2000 to 5000, after coating the dried film surface with platinum by evaporation. Drying of the hydrated film was performed either at room temperature and atmospheric pressure in air (ambient condition) or after freeze-drying at 77 K. No special care was taken during freeze-drying to avoid contamination, for instance, with hydrocarbon from the rotary pump.

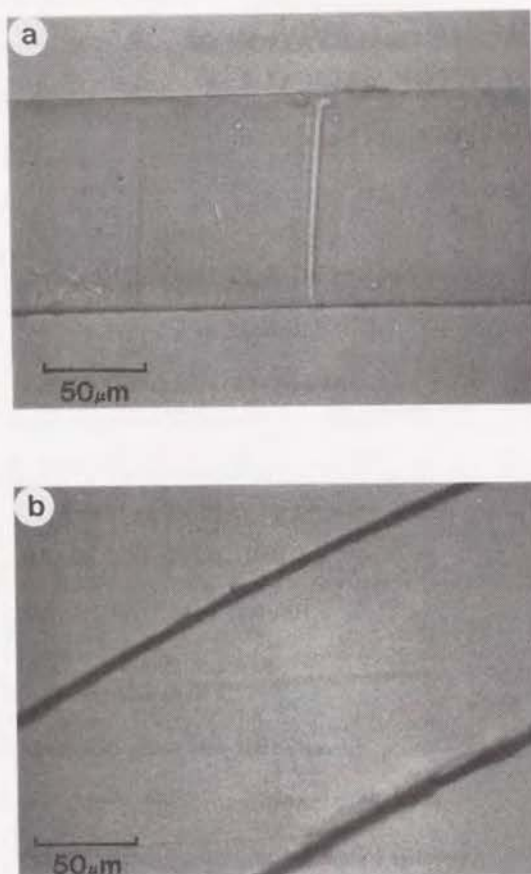


Fig. 1. Optical micrograph of the cross-section of the acrylamide-grafted polyurethane films (graft density = $150 \mu\text{g}/\text{cm}^2$); (a) virgin and (b) AAm-grafted.

RESULTS

Surface Grafting

Figure 1 shows the optical microscopic photograph of the cross-section of an AAm-grafted polyurethane film after staining the AAm polymer with Skyblue 6B. As the surface of polyurethane film is readily oxidized by ozone under formation of polymer peroxides[13], a high density of polymer chains can be readily grafted onto the oxidized polyurethane surface, compared to other polymeric materials. The AAm polymer grafted onto the polyurethane film shown in Figure 1 amounts to $150 \mu\text{g}/\text{cm}^2$. As can be seen, the graft layer is localized at the surface region with the thickness of several μm . To study the chemical structure of the graft layer, XPS and ATR FT-IR spectroscopy were conducted for the surface-grafted polyurethane film. Figure 2 shows examples of XPS measurement on C_{1s} level. The peaks at 285.0, 288.0, and 289.5 eV are assigned to C_{1s} of $-\text{CH}_2\text{CH}_2-$, $-\text{CONH}-$, and $-\text{OCONH}-$, respectively. The starting polyurethane film has $-\text{CH}_2\text{CH}_2-$, $-\text{OCONH}-$, and $-\text{OCH}_2-$ which probably appears at 286.0 eV, while the AAm homopolymer has only $-\text{CH}_2\text{CH}_2-$ and $-\text{CONH}-$. It is seen that the $-\text{CONH}-$ peak greatly increases with an increase in graft density, in contrast to $-\text{OCH}_2-$. If XPS analyzes practically only the surface region within about 5 nm from the outermost surface[17], it follows that the graft layer does not consist of PAAm chains alone even within 5 nm. In other words, as graft polymerization proceeds further, a small fraction of polyurethane chains will incorporate from the bulk phase into the graft layer. A similar result was observed for PET film graft-polymerized with AAm[18].

ATR FT-IR spectra were measured for the DMAA-grafted polyurethane film. The DMAA monomer was more easily graft polymerized than the AAm monomer which was difficult to get a graft density larger than $50 \mu\text{g}/\text{cm}^2$. The integrated relative intensity ratio based on the differential spectra of carbonyl between the virgin and the DMAA-grafted film from 1732 to 1566 cm^{-1} , assigned to the grafted DMAA polymer chain, was plotted against the graft density in Figure 3, together with the observed optical density at 615 nm. The grafted films were stained with Skyblue 6B prior to the measurement of the optical density.

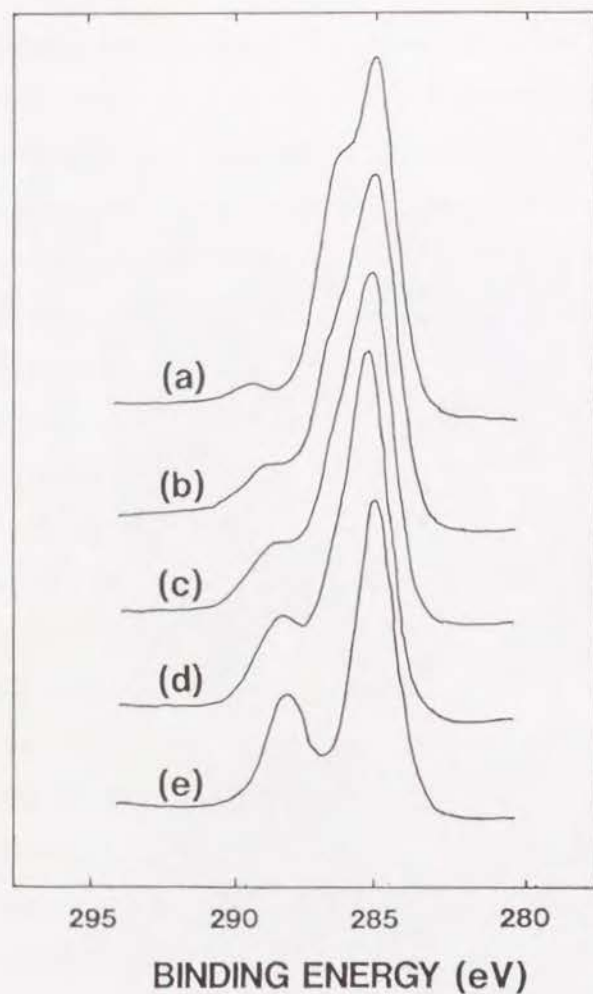


Fig. 2. C_{1s} XPS spectra of virgin polyurethane film (a), acrylamide homopolymer (e), and acrylamide-grafted polyurethane films (b-d); graft density ($\mu\text{g}/\text{cm}^2$): b, 8; c, 14; d, 26.

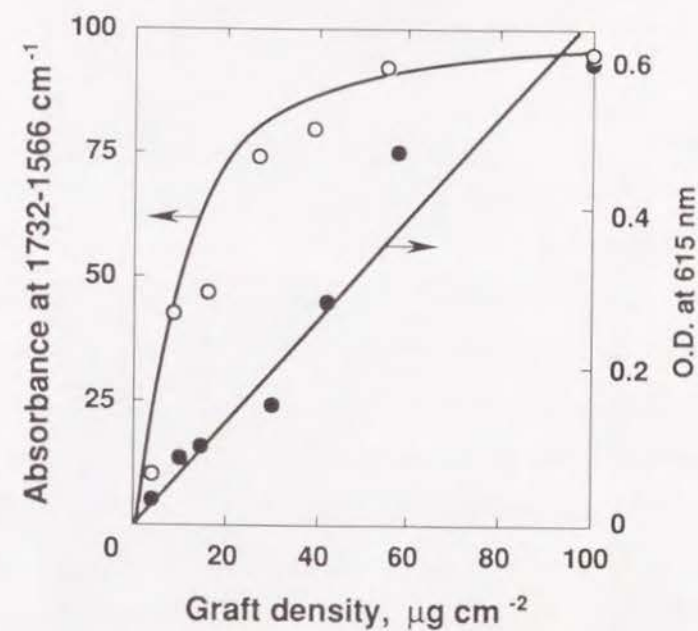


Fig. 3. Ratio of integrated absorbance of FT-IR spectra from 1732 to 1566 cm^{-1} and optical density at 615 nm (OD_{615}) for dimethyl acrylamide-grafted polyurethane films. OD_{615} was measured after staining the film surface with Skyblue 6B.

As can be seen from Figure 3, the intensity ratio increases with the increasing graft density, at least in its small range. The saturation seen at the graft density larger than $50 \mu\text{g cm}^{-2}$ is probably because the graft polymerization of DMAA took place very deeply to the polyurethane substrate as the ATR FT-IR analysis gives information on the surface structure within several μm . On the other hand, the OD_{615} value increased almost linearly with the increasing graft density up to $100 \mu\text{g cm}^{-2}$.

Surface Lubrication

Lubrication of the grafted polymer surface was evaluated by determining the μ value against a glass plate although it is far different from the tissue, simply because glass plate is most commonly used to determine μ of polymer surfaces. The ungrafted polyurethane surface is extremely hard to determine the μ value against the glass plate if water is absent, because a strong adhesive force is operative between the film surface and the glass plate. This is in contrast to other polymeric materials such as polypropylene, nylon 6, and ethylene-vinyl acetate copolymers[15]. However, the μ value of AAm-grafted film was measurable even in the absence of water and found to be 0.3, when the graft density was higher than $10 \mu\text{g cm}^{-2}$. This μ value is virtually equal to that for polypropylene. The grafted polyurethane film showed a remarkable decrease in friction against a glass plate when hydrated. It was smaller than 0.05 when the graft density exceeded $20 \mu\text{g cm}^{-2}$. When touched with fingers, the hydrated surface with μ of 0.05 gave us very slippery feeling.

SEM Observation

The above XPS and ATR-IR measurements on the film surface were all done at the dried state. If the grafted surface comes in contact with plenty of water, the graft layer is swollen with water, resulting in expansion of graft chains, which, however, cannot dissolve into water, because they are tethered to the water-insoluble substrate through covalent bonding. Figure 4 shows the SEM micrographs of the virgin and the DMAA-grafted films with the graft density of 50 and $100 \mu\text{g cm}^{-2}$. Prior to SEM observation, all the surfaces were air-dried under the ambient condition. As can be seen, no significant difference was observed among

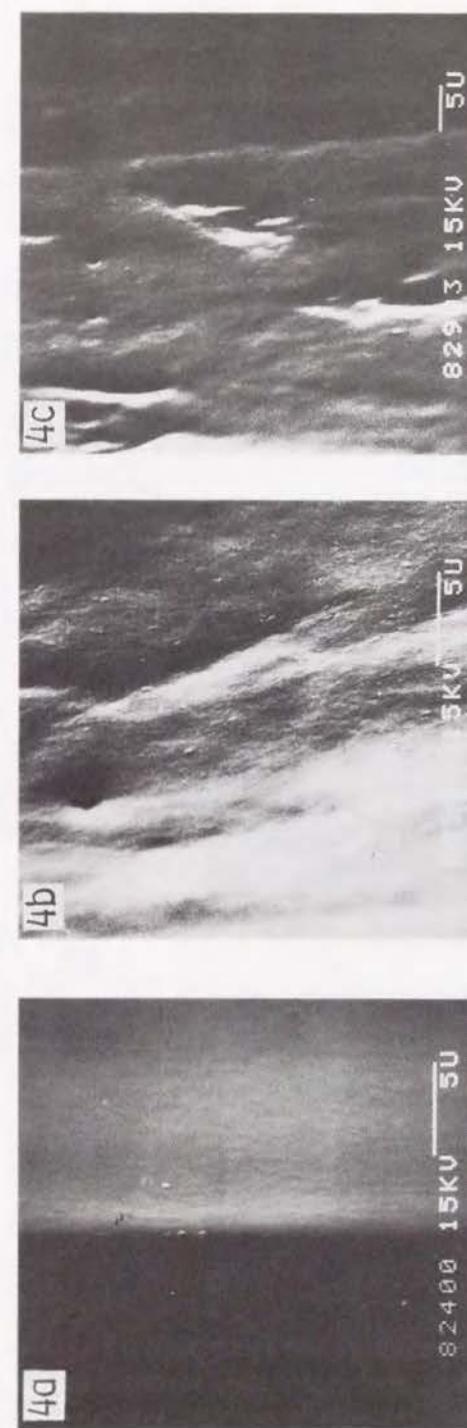


Fig. 4. Scanning electron micrographs of virgin polyurethane (a) and dimethyl acrylamide-grafted polyurethane films (b and c) dried under the ambient atmosphere; graft density ($\mu\text{g cm}^{-2}$): b, 50; c, 100. Bars = $5 \mu\text{m}$.



Fig. 5. Scanning electron micrographs of dimethyl acrylamide-grafted polyurethane freeze-dried after immersion in water; graft density ($\mu\text{g}/\text{cm}^2$): a, 30; b, 50; c, 100. Bars = $5\mu\text{m}$

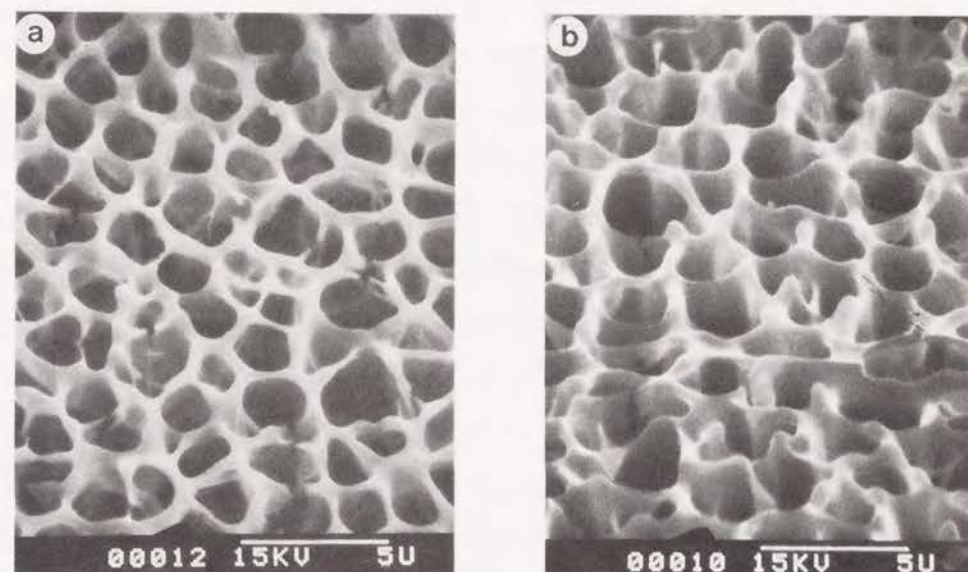


Fig. 6. Scanning electron micrographs of acrylamide-grafted poly(ethylene terephthalate) films freeze-dried after immersion in water; graft density = $400 \mu\text{g}/\text{cm}^2$; a, 30 view; b, 60 view. Bars = $5\mu\text{m}$

these three films. On the contrary, when the grafted films were subjected to freeze-drying following hydration by immersion in water, the SEM micrographs gave a textured pattern quite different from those of air-dried. They are shown in Figure 5. The textured structure is more clearly observed, as the graft density increases. It is interesting to note that the surface of grafted films was transparent when air-dried, similar to that of virgin film, whereas the grafted films became opaque upon freeze-drying. However, the dried opaque surface became again transparent without any textured structure when stored in air for a short time like 10 min, unless the surface was covered with thin metallic coating for SEM observation. As the freeze-dried surface without metal coating was so unstable, the measurements of XPS and ATR-IR were difficult to conduct within such a short time.

Similar topography was observed on AAm-grafted PET films having graft densities higher than $50 \mu\text{g cm}^{-2}$. Figure 6 shows an example of SEM micrographs of AAm-grafted PET films with the graft density of $400 \mu\text{g cm}^{-2}$, taken at 30° and 60° angular view.

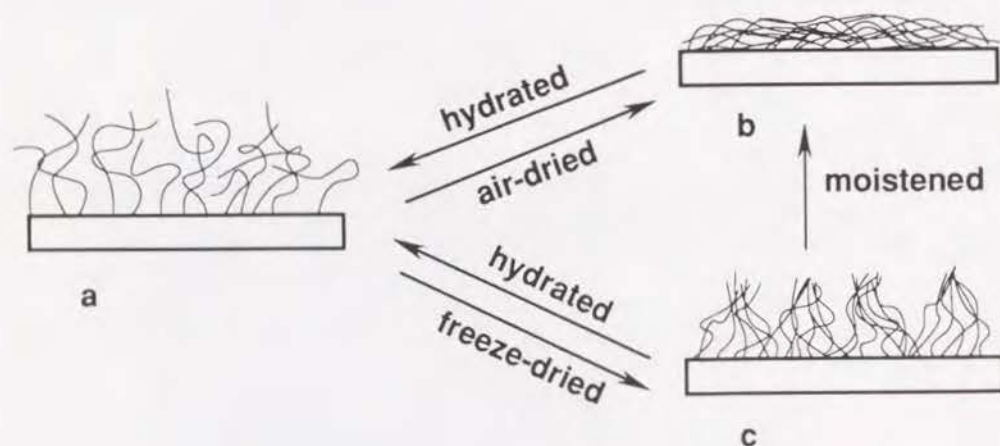


Fig. 7. Schematic representation of the surface structure of polyurethane film grafted with water-soluble polymers in water (a), after air-drying (b), and after freeze-drying (c).

DISCUSSION

Segmented polyurethane is a good thermoplastic elastomer without additives such as plasticizer and chemical crosslinker. Therefore, it is employed in the medical field, for instance, for cardiovascular devices, nutrition catheters, and guidewire coating. Such biomaterials are generally desired to have a slippery surface to allow easy insertion and reduce mechanical damage to tissues in direct contact. However, a highly elastic polyurethane surface will interact strongly with an opposing surface in contact under pressure, leading to significant adhesion and displacement. As a result, complicated hysteresis occurs in a cycle of deformation and recovery during the frictional motion against a solid surface[19]. On the contrary, the polyurethane surface grafted with water-soluble polymers can retain lots of water molecules on the surface for a long time. Indeed, the freeze-dried surface was unstable in air even at room temperature, probably because of the immediate reorientation of grafted polymer chains through quick absorption of water from the surrounding atmosphere. Although the grafted surface may interact less strongly with another solid surface than the ungrafted, it does not become slippery unless water is present, because there exists no lubricant at the interface between the two solid surfaces.

It is important to note that a lack of lubricity in a hydrophilic polymer blend or hydrogel coating usually results from insufficient degree of hydration and/or restricted chain mobility due to either excessive complexation or excessive cross-linking of the hydrophilic polymer. The presence of a sufficiently large population of mobile water molecules and hydrophilic polymeric chains on the surface is believed to be an essential element to ensure a satisfactory lubricity. As demonstrated above, the graft layer does not consist of pure graft chains but slightly mixed with the substrate polymer and the topography of the graft layer depends on the graft density as well as on the surrounding environment. The possible configurations of graft chains on the surface may be schematically represented as shown in Figure 7. When a surface having highly hydrated chains, as shown in Figure 7(a), is slowly air-dried, all the graft chains must evenly lie down on the surface as illustrated in Figure 7(b), exhibiting transparency but no significant difference from the ungrafted substrate when observed by

SEM. However, when the hydrated graft chains are subjected to freeze-drying, a textured structure should be formed as depicted in Figure 7(c), because partial aggregation of chains will take place in the graft layer upon freezing of water as the grafted chains are mobile enough although attached to the substrate surface. It is a well-known fact that, when an aqueous solution of polymer is frozen, microscopic phase separation takes place as a result of ice formation[20]. An addition of glycerin to water for hydration of the graft layer had no effect on the freeze-dried structure. Critical point drying of the hydrated surface having densely grafted chains gave a SEM micrograph similar to those by freeze-drying. Absorption of atmospheric water may allow the aggregated polymer chains to reorient, probably because the absorbed water functions as solvent of the aggregated chains to permit sufficient mobility for rearrangement to a more thermodynamically stable state to occur.

Ratner and his coworkers reported that a textured surface was seen on SEM micrographs of low-density polyethylene films graft-copolymerized using 2-hydroxyethyl methacrylate and ethyl methacrylate by a radiation-induced technique[21,22]. However, the textured structure is quite different in magnitude and appearance from those shown in Figures 5 and 6. They explained the textured surface in terms of preferential grafting to the amorphous region of polyethylene. On the other hand, Lazare et al showed the topography similar to ours for the PET film subjected to photoablation with far ultraviolet excimer laser[23,24]. When treated with ozone or UV exposure, neither polyurethane nor PET film exhibited any significant difference from the non-treated, indicating no significant erosion in the course of surface graft polymerization. It seems likely that the textured surface seen in Figures 5 and 6 is due to the build-up of closely lumped graft chains formed in the graft layer in the course of freezing, if the thickness of graft layer and the graft density are sufficiently large.

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APPLICATION OF LUBRICIOUS SURFACES TO DRAG REDUCTION

INTRODUCTION

It would be interesting if the lubricating surface described so far can be applied, for instance, to the wall of pipe transporting fluid or to the surface of a boat or an aircraft to increase the volume flow of fluid or the craft speed. In 1948, Toms [1] reported the flow of linear polymer solutions through tubes at large Reynolds numbers. In his experiment, the frictional drag in the turbulent flow of chlorobenzene decreased when a low amount of PMMA was added in the solvent. Today, the phenomenon of such "drag reduction" system is often called "Toms effect". Application of this phenomenon was first directed to oil transportation pipeline industry as it had the potential for reducing the energy required for oil delivery. In this case, injection of only a low concentration of high-molecular-weight polymers in the turbulent flow led to a substantial drag reduction in the pipelines. Interthal[2] demonstrated a pressure drop along the pipeline of 3000 m length filled with flowing water by adding polyacrylamide. However, for longer pipelines it was no more applicable because the added polymer underwent significant degradation due to the thermal and mechanical chain scission over the long distance.

The drag reduction has been accounted for in terms of decreasing turbulence, wall effect (not related to the surface nature of pipe, but to the shear thinning wall layer), adsorption effect, stretching of polymer molecules in flow, and so forth[3].

The surface of many fishes such as eel is very slippery in the presence of water, while marine mammals like porpoises move through the water at high speeds. Scientists have tried to learn from these animals how they can attain such a slippery surface and how they can swim through water avoiding frictional drag. As a result, several techniques for drag reduction systems have been proposed imitating natural animals, since such systems have been greatly desired in the fields of marine, aerodynamics, fluid transportation, and biomedical

engineering. It has been often postulated that a ship with an identical surface to that of dolphin's skin could attain a similar sailing speed. Kraemer [4] had tried to apply an elastic material on a ship-like model and evaluated the effect measuring the drag coefficient between the ship surface and sea water. Although he concluded that a drag reduction effect was observed in the restricted range of Reynolds' number, the effect could not be found over the wide range of the turbulent flow.

On the other hand, many experimental results indicate that riblets are effective in reducing the skin friction drag [5]. Walsh intensively studied the drag reduction of turbulent boundary layer using riblets[6-8] and concluded that the maximum drag reduction by the V-groove riblet was dependent on the height and spacing of the riblets in law-of-the-wall variables, regardless of the free-stream Reynolds' number or upstream boundary-layer history. The V-groove riblet having the optimal structure in height and spacing exhibited 7 to 8 % drag reduction. Riblet materials[9] and a ciliated material [10] were also disclosed in patents. Gould et al. [11] reported that water flow through a tube treated with hydrophilic polyurethane for surface lubricity was found to increase the flow by 22 % as compared to the flow through the untreated tube.

This chapter is concerned with the effect of surface lubricity on the drag reduction using a surface-grafted HDPE and polyurethane tube.

EXPERIMENTAL

Graft Polymerization

Graft polymerization of HDPE film with acrylamide was performed by the method described elsewhere[12]. A glow discharge reactor, Model LCVD-12 type manufactured by Shimadzu Corp., Kyoto, Japan, equipped with a bell-jar-type reaction cell, was used for the plasma pretreatment of the HDPE film. The film was fixed to a stainless steel sample holder placed between two electrodes, to which RF power was applied at a frequency of 5 KHz. The holder was rotated at 68 rpm by a motor to ensure homogeneous plasma treatment over the whole film surface. The pressure in the bell jar was first reduced to 10^{-3} torr or lower, and subsequently Ar gas was introduced at a flow rate of about 20 ml/min. When the pressure

in the bell jar was maintained at about 0.03 torr of Ar, the films were subjected to glow discharge mostly for 15 sec. These Ar plasma pre-treated films were then exposed to dry air prior to grafting. Following the plasma treatment, the HDPE film was placed in a Pyrex test tube containing a deaerated monomer solution. The mixture was then kept at 65°C to effect graft polymerization. To remove the homopolymer formed, the grafted film was first washed with running tap water and then immersed in distilled water at 70°C for 20 h under continuous stirring. On the other hand, surface graft polymerization onto the inner wall of polyurethane tube (ID = 0.65 mm, length = 200 cm) was carried out with an ozone method. The inner wall of polyurethane tube was passed through with ozone-oxygen mixture with the aid of aspirator. Ozone was generated from oxygen by an ozonizer(O-1-2 type, Nippon Ozone Inc., Tokyo) at an ozone concentration of approximately 0.2 vol% in oxygen. Following ozone passage, the inner wall of polyurethane tube was filled with deaerated aqueous solution of monomer and kept at 65°C for 1 h. The homopolymer formed inside the tube was removed by passing distilled hot water (about 70°C) for 20 h with the help of aspirator.

Measurement of Friction Drag

In order to maintain a constant turbulent flow over a wide range of Reynolds' number for a long period of time, a large scale flowing system was constructed as shown in Figure 1. The grafted HDPE film was attached on the inner wall of the test pipe (I.D. = 19.2 cm, length = 60 cm) inserted at the midst of the flow path as demonstrated in Figure 2. Flow test was conducted with the turbulent flow at the Reynolds' number of $(1.0 - 7.0) \times 10^4$ and the flow rate of 0.7 - 4.5 m/s. Friction factor λ was calculated based on the Plandtl-Karmer Equation(Eq. 1).

$$1/\sqrt{\lambda} = 2.0 \log Re \sqrt{\lambda} - 0.8 \quad (1)$$

A flow rate of water through the polyurethane tube in the range of laminar flow (Reynolds'

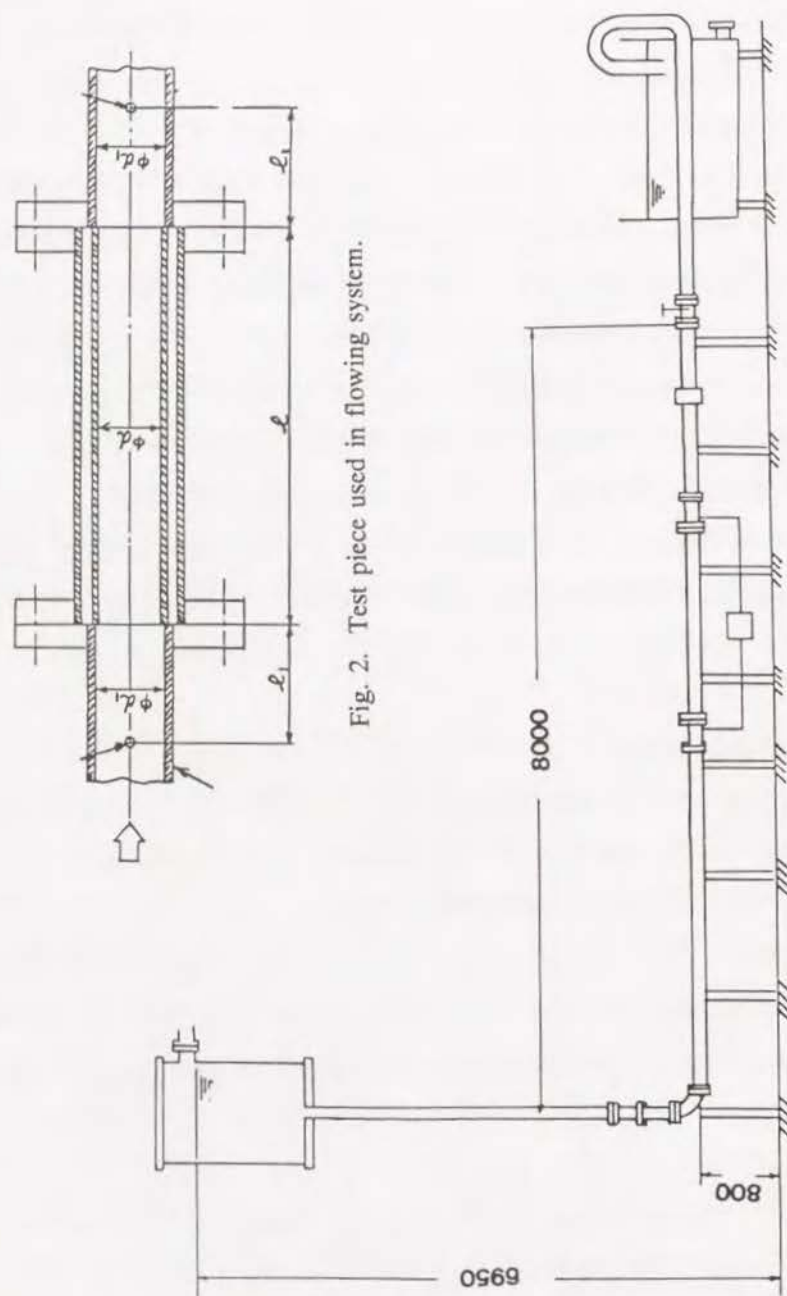


Fig. 2. Test piece used in flowing system.

Fig. 1. Flowing system to determine a friction factor of test pipe in turbulent flow.

number ranging less than 10) was measured at constant temperature $25^{\circ}\text{C} \pm 0.1$. The efficiency of drag reduction can be postulated accounting for the Hagen-Poiseuille's equation.

$$J = \pi r^4 \Delta P / 8 \eta l \quad (2)$$

where J is the flux of liquid flow, ΔP is the difference of pressure between inlet and outlet, η is the viscosity of liquid, and r and l are the radius and length of tube, respectively.

RESULTS AND DISCUSSION

The calculated friction factor λ at the various Reynolds' numbers was plotted in Figure 3. As can be seen, the walls of the smooth pipe with and without the grafted film both obeyed exactly the Prandtl-Karmer equation. It follows that the attached film influences neither interference nor drag reduction of the liquid flow, indicating that the surface structure of the wall does not play a significant role on drag reduction, because the slip between the wall surface and the fluid is insignificant. The coefficient of friction of the surface-grafted film did not change even after the flow test was run for more than 60 h at the flow rate of 3.4 cm/s, Reynolds' number of 6.4×10^4 , and the shear wall stress of 30 N/m^2 .

On the other hand, a polyurethane tube (I.D. = 0.61 mm length = 120 cm) whose inner wall was surface-grafted with acrylamide and DMAA, always retarded the laminar flow at Reynolds' numbers less than 10, although the inner wall became hydrophilic and slippery. Since the pressure drop associated with flow in pipe or tube may be caused by many factors such as shape (especially at the inlet part), curvature, temperature, and contaminants, absolutely correct data are difficult to obtain by such a simple experiment. However, simply assuming that the flow retardation is caused by narrowing of the inner diameter of the tube due to the swelling of the surface graft layer, it is possible to use Hagen-Poiseuille's equation (Eq. 2) to check the validity of this correlation under laminar flow. The narrowed diameter (ΔD) of tubes was tabulated in Table I, together with contact angle of inner wall determined with a capillary-rise method. As can be seen, the effective diameter calculated based on narrowing of the tube inner diameter due to the swelling of the graft layer was several

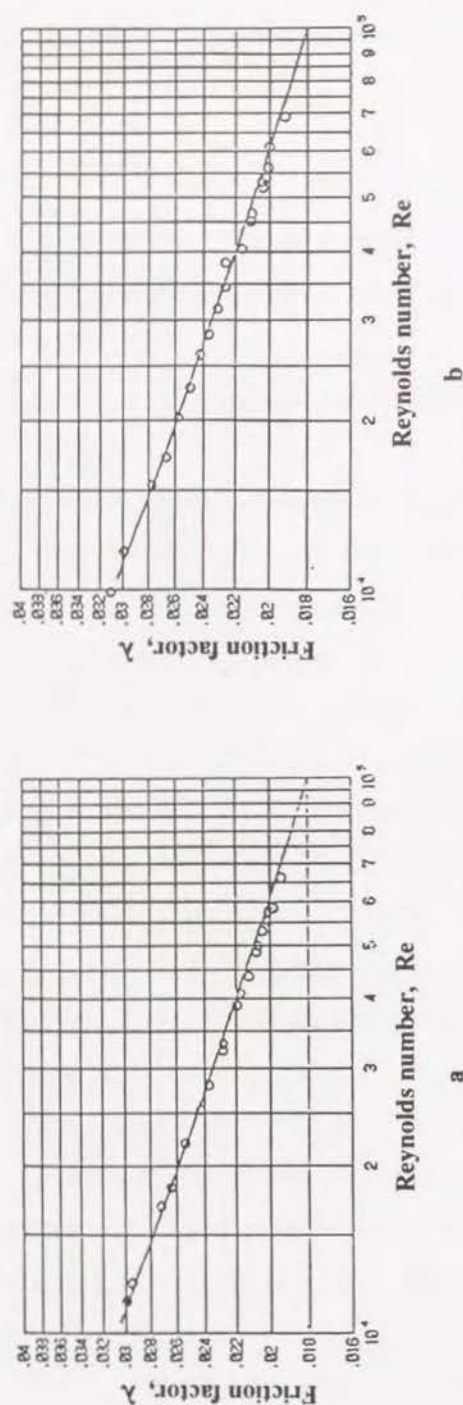


Fig.3. Plots of friction factors calculated for the pipe untreated (a) and surface-grafted with acrylamide (b) at various Reynolds numbers. Straight line shows the Plandtl-Karmer Equation.

Table I Contact angles of inner wall of tube and narrowing of tube inner diameter (ΔD) due to the swelling of the graft layer in a laminar flow.

PU tube	tube length, cm	O ₃ treatment time, min	θ^a deg	Re ^b	ΔD μm
untreated	120.6		63-75	5.3-7.6	0
exposed to O ₃	121.4	10	62-69	6.1-8.8	
AAm-grafted	118.2	10	19-30	5.6-7.9	9.0
	120.7	5	-	5.8-8.2	7.5
	121.0	2	-	5.0-7.2	6.6
DMAA-grafted	94.3	5	23-27	6.5-9.5	8.6

a) Maximum and minimum values of contact angle of the inner wall determined by a capillary-rise method are given.

b) Range of Reynolds' number during the flow test is given.

micrometers. This value was in agreement with that estimated from the thickness of the swollen graft layer obtained from the staining.

It is known that the surface of boats and bathing suits, applied with a mucous material, can achieve a higher speed at the same energy. This increase in speed is not due to the wall slip, but to removal of the mucous material in the course of movement. Although a similar mucous layer exists at the region between the grafted surface and water, the grafted chains are tethered to the solid substrate through covalent bond inhibiting removal of the mucous layer. Probably the lubricating polymer surface is applicable to drag-reduction systems, but any effect of drag reduction was hardly observed on the results obtained in this chapter.

Although there are a few reports which have succeeded in improving the turbulent flow, problems still remain unsolved in the drag-reduction systems.

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Summary

In Chapter I of Part I, contact angles against water droplet on polymer films such as cellulose, polyethylene, and other widely used polymers were determined with three different methods. They included the telescopic sessile drop method, the laser beam goniometry, and the Wilhelmy plate technique. Their advantages and disadvantages were compared with each other based on the results of the contact angle measurement. The conventional telescopic method was the simplest in measurement, while the laser beam goniometry and the Wilhelmy method were much advantageous over the telescopic sessile drop goniometry in accuracy and reproducibility. The most abundant information on the surface properties of polymers could be obtained by the Wilhelmy plate method. For hydrophobic surfaces, a hysteresis loop was clearly different between the advancing and the receding scanning when the measurement was performed with the Wilhelmy method. It was observed that the telescopic sessile drop method and the laser beam goniometry method gave identical contact angles on a wide variety of surfaces ranging from hydrophobic to hydrophilic in nature. The experimental error associated with the laser beam goniometry was smaller than that obtained from the telescopic sessile drop method. The mean contact angles derived from the Wilhelmy plate method were also in good agreement with those derived from the other two methods.

In Chapter II, surface analysis on UV irradiated polymer films was performed utilizing a combination of the quantitative analysis of peroxides with 1,1-diphenyl-2-picrylhydrazyl (DPPH) and XPS spectroscopy as well as the contact angle measurement. The use of UV irradiation seems to be an excellent method for surface modification of polymeric materials, because of great simplicity and cleanness of its treatment. Polymer films employed in this Chapter were nylon 6, polypropylene (PP), ethylene-vinyl acetate copolymer, and other commonly available films. It was found that peroxides were introduced on the surface of these polymer films upon UV irradiation. An XPS study revealed clearly the UV-irradiated surfaces to be oxidized. In addition, formation of peroxides was strongly suggested by the reaction of irradiated films with DPPH. The increase in peroxide concentration analyzed by the DPPH method for nylon 6 was larger than that of O_{1s}/C_{1s} ratio determined by XPS spectra. It is likely that the nylon 6 film is oxidized to the depth much deeper than 5 nm

from the surface, when UV irradiation is prolonged. The surface of UV-irradiated polypropylene film became less wettable toward water than that of nylon 6 film, although the peroxide formed on the PP film was higher than that on the nylon 6. As the pure PP film does not absorb any light of UV wavelength, the PP film would be more deeply oxidized by UV radiation than nylon 6 film. Poly(methyl methacrylate) and high density polyethylene were more stable to UV light than nylon 6 and PP.

In Chapter III, graft polymerization of acrylamide was attempted onto the surface of films preirradiated with UV radiation. The films employed were nylon 6, PP, and EVA with different VA contents. Following UV irradiation in air onto films without photosensitizer, they were placed in monomer solution, degassed, and then heated to 50° C to effect the graft polymerization. After rigorous removal of homopolymers, polyacrylamide chains were found to be grafted in the surface region of the films to amounts up to several hundred micrograms per square centimeter of films. As was demonstrated in Chapter I, the initiator responsible for the graft polymerization is peroxides generated at and near the film surfaces upon UV irradiation. The grafted films became very hydrophilic, in contrast with the films UV-irradiated but not yet grafted. For instance, the contact angles of the PP films unirradiated and UV-irradiated for 5.5 h were 87 and 84°, respectively, whereas the film grafted to 120 μgcm^{-2} had a contact angle as low as 21°. Graft polymerization of AAm onto the nylon 6 films preirradiated with UV took place as effectively as or more effectively than that for PP films. Over the range of the exposure time studied, the UV irradiation had little effect both on the tensile strength and the elongation at break of the films. The surface grafting using UV preirradiation seems to be an application of the active species generated upon UV irradiation in the early stage where polymer chain does not suffer significant cleavage yet. The graft density obtained for ethylene-vinyl acetate copolymer films having different vinyl acetate contents was dependent on the VA content.

In Chapter IV, electrostatic properties on polymer surface was studied. A polystyrene film, a poly(ethylene terephthalate) (PET) film, and PET fabrics were UV-irradiated or subsequently surface-grafted with various hydrophilic monomers. Their electrostatic properties were examined by measuring the triboelectric charges generated upon mechanical rubbing of these materials and by following the decay of the charges generated upon exposing

the polymeric materials to a high electric field. The UV-irradiated polymers carried lower electrostatic charges than those unirradiated when their surfaces were rubbed with cotton fabrics under the same conditions. The generation of triboelectric charge depended on both the surface hydrophilicity and the past history of the specimens. Although hydrophilic groups introduced on the polymer surface by UV exposure exhibited little effect on decaying of the electrostatic charge, polymeric materials grafted with a large amount of water-soluble polymers, especially with ionic polymers, showed lower triboelectric generation and faster decay of the static charge.

Grafted surfaces with water-soluble monomers often exhibited an adhesion force toward the contacting countersurface. In Chapter V, the adhesive property of grafted polymer surface was studied. A polyester film was employed and the surface was graft-polymerized with various water-soluble monomers by combination of plasma pretreatment and photoirradiation. The grafted surfaces showed strong adhesion to another non-grafted or grafted films when brought into direct contact in the presence of water and subsequently dried. The adhesion force depended on the hydrophilicity of the adhering surfaces and the graft density. The film having larger graft density generally showed stronger adhesion in the final stage of drying, but it took longer time to achieve high adhesion because of larger amounts of water existing in the interfacial region between the two surfaces. On the other hand, substantial adhesion was obtained almost instantaneously upon contact when one was grafted with an anionic polymer and the other with a cationic polymer. Adhesion between similarly charged surfaces was very weak in the beginning of drying, probably because of the electrostatic repulsion between the charged groups.

In part II, lubricating polymer surface was intensively studied. Chapter VI dealt with the principles and problems associated with polymer surface lubrication using films of nylon 6, polypropylene, and ethylene-vinyl acetate copolymers. They were graft polymerized with acrylamide or dimethylacrylamide to render the hydrated surfaces slippery. The graft polymerization altered the films from the hydrophobic and non lubricating to the hydrophilic and slippery surfaces. To evaluate the surface lubricity, the coefficient of friction (μ) against a glass plate in water was determined with the help of a tensile testing machine. The μ value of the films surface-grafted with acrylamide up to 30 μgcm^{-2} was reduced to less than 0.05,

regardless of the substrate polymers.

One of the most promising applications of lubricious polymer surface would be for biomedical devices such as guidewire, catheter, and endoscope. Chapter VII devoted to develop low-frictional catheters. Photo-induced graft polymerization of N,N-dimethylacrylamide (DMAA) was performed onto films and tubes of ethylene-vinyl acetate copolymer(EVA) and poly(vinyl chloride)(PVC). Although no significant difference was observed in surface lubrication between the EVA film and the tube, the latter required an additional procedure for the graft polymerization, that is, removal of air trapped inside the tube. The surfaces of EVA and PVC tubes grafted with DMAA were found to exhibit frictional forces around 0.5 N against a PVC and a silicone surface under wet conditions, whereas the frictional force of the ungrafted tubes against the same substrates was 10 and 20 N for PVC and EVA, respectively.

In the course of studies on the lubricious surfaces modified by graft polymerization, a peculiar textured structure was found by scanning electron microscopic(SEM) observation on polymer films surface-grafted with water-soluble polyacrylamide and poly(N,N-dimethylacrylamide). SEM on the grafted surfaces revealed different profiles, depending on the graft density as well as the process of drying prior to the SEM observation. There was no significant difference between the virgin and the surface-grafted film, when air-dried under the ambient condition. However, when the surface was freeze-dried following immersion in water, the SEM micrograph of surface-grafted films exhibited a textured structure, probably due to partial aggregation of the water-soluble graft chains to micro-domain, caused by freezing of water in the graft layer. In Chapter VIII, the structure of these surfaces was discussed.

It would be interesting if the lubricating surface described so far can be applied to drag reduction systems. The drag reduction has been accounted for in terms of decreasing turbulence. In Chapter IX, the effect of surface lubrication of pipe on the drag reduction was examined. However, the walls of the smooth pipe with and without the grafted film both obeyed exactly the Prandtl-Karmer equation. It indicates that the attached film influences neither interference nor drag reduction of the liquid flow. It is likely that the surface structure of the wall does not play a significant role on drag reduction, because the slip between the

wall surface and the fluid is insignificant. On the other hand, a polyurethane tube whose inner wall was surface-grafted with acrylamide and DMAA, always retarded the laminar flow at Reynolds' numbers less than 10. The effective diameter calculated based on the narrowing of the tube inner diameter due to the swelling of the graft layer was several micrometers.

List of Publications

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| Chapter I | Uyama,Y., Inoue,H., Ito,K., Kishida,A., and Ikada,Y., "Comparison of different methods for contact angle measurement", <i>J. Colloid Interface Sci.</i> , 141 (1), 275-279(1991). |
| Chapter II | to be submitted |
| Chapter III | Uyama,Y. and Ikada,Y., "Graft polymerization of acrylamide onto UV-irradiated films", <i>J. Appl. Polym. Sci.</i> , 36 , 1087-1096 (1988). |
| Chapter IV | Uyama,Y. and Ikada,Y., "Electrostatic properties of UV-irradiated and surface grafted polymers", <i>J. Appl. Polym. Sci.</i> , 41 , 619-629 (1990). |
| Chapter V | Chen,K.-S., Uyama,Y., and Ikada,Y., "Adhesive-free adhesion of grafted surfaces with different wettabilities", <i>J. Adhesion Sci. Technol.</i> , in press. |
| Chapter VI | Uyama,Y., Tadokoro,H., and Ikada,Y., "Surface lubrication of polymer films by photo-induced graft polymerization", <i>J. Appl. Polym. Sci.</i> , 39 , 489-498 (1990). |
| Chapter VII | Uyama,Y., Tadokoro,H., and Ikada,Y., "Low-frictional catheter materials by photo-induced graft polymerization", <i>Biomaterials</i> , 12 , 71-75(1991). |
| Chapter VIII | Inoue,H., Uyama,Y., Uchida,E., and Y.Ikada,Y., "Scanning electron microscope observation of lubricious polymer surface for medical use", <i>Cells and Materials</i> , 2 , 21-28 (1992). |
| Chapter IX | to be submitted. |

Acknowledgement

The present study was carried out under the continuous guidance of Dr. Yoshito Ikada, Professor of Research Center for Biomedical Engineering, Kyoto University from 1983 to 1992.

The author is deeply indebted to Professor Yoshito Ikada for his constant guidance, encouragement, valuable discussion, and detailed criticism on the manuscript throughout the present work.

General acknowledgment is due to Professor Ken Ikeuchi, Associate Professor Toshio Hayashi, and Dr. Suong-Hyu Hyon of the Center for their significant advises and intimate guidance.

The author is also very much indebted to Dr. Takehisa Matsuda and Dr. Hiroo Iwata of National Cardiovascular Center Research Institute for their appreciable advises, invaluable corporation, notable suggestion, and the use of XPS instrument.

The author is very much grateful to Dr. Daniel Graiver, Dow Corning Corp., Dr. Kang En-Tang, National University of Singapore, and Dr. Ko-Shao Chen, Department of Materials Engineering, Tatung Institute of Technology, and Miss Emiko Uchida of the Center for proof reading of manuscripts, co-working for the present studies, many fruitful discussion, and valuable advises.

The author wishes to express his thanks to Dr. Teiji Hayakawa, Mitsui Engineering and Shipbuilding Co., Ltd., for his kind help and advice, especially for constructing an instrumentation of large-scale pipeline for turbulent flow measurement.

The author is also grateful to Dr. Masakazu Suzuki, Gunze Inc., Dr. Akio Kishida, Kagoshima University, Mr. Hideki Tadokoro, Japan Medical Supply Inc., and Mr. Hiroyuki Inoue, Nissho Inc., for their kind help for co-working for the present work.

The author likes to take the opportunity to extend his heartily thanks to Dr. Yasuhiko Tabata and other investigators of Professor Ikada's laboratory for their continual encouragement, support, and kind help throughout the present study.

Assisting in the typing and proof reading of the manuscripts by Mrs. Emiko Uyama, his wife, is also appreciated.