LOW-FRICTIONAL HYDROPHILIC SURFACE BY PLASMA-INITIATED GRAFT COPOLYMERIZATION

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The aim of this study is to prepare materials with lubricious surfaces to be used in the manufacture of invasive medical devices such as catheters thus to minimize injury and patient discomfort during application. A water-soluble polymer, poly(N,N-dimethylacrylamide) (PDMAA), has been grafted onto the films of poly(ethylene terephthalate), polyethylene and polypropylene to render their surfaces lubricious. After exposing the films to argon plasma, the films were allowed to react with DMAA vapor to produce the graft polymer (plasma-graft). PDMAA grafted surfaces, characterized by ESCA and IR, had a low friction coefficient when wet, and the lubricity was durable. The plasma-graft onto the surfaces pretreated with benzoyl peroxide enriched the PDMAA at the outermost surface and made the surface more lubricious than untreated ones.

1. Introduction

Polymeric materials such as polyolefin, polyester and polyurethane are widely used for manufacturing catheters and other medical devices; such materials are inherently non-lubricious. It is therefore desirable that they are fabricated to have a low surface friction. Such a lubricious surface would facilitate insertion or withdrawal of a medical device, such as catheter, into or out of blood vessels or urethra, thus minimizing injury, inflammation and patient discomfort.

A hydrophilic lubricious surface is a common feature in the living system. For example, most of the surfaces of sea creatures and living tissues of mammals are naturally lubricious in a hydrated state. These surfaces are covered with a highly hydrophilic natural polymer which reduce friction in motion and protect tissue damage.

A variety of approaches have been undertaken to develop a hydrophilic lubricious surface for medical devices.[1, 2] These are mainly based on the techniques of binding water-soluble polymers onto polymer surfaces. Surface grafting of hydrophilic monomers onto polymer substrate is an effective technique to render the hydrated surface lubricious. Uyama *et al.* obtained a lubricious surface by grafting acrylamide or N, N-dimethylacrylamide (DMAA) using photo-induced graft copolymerization technique.[3,4]

Low-temperature plasma (LTP) generates radicals on polymer substrate, and the radicals can act as sites for initiating graft copolymerization.[5-8] In the present work, vapor-phase plasma-initiated graft copolymerization (plasma-graft) with or without benzoyl peroxide (BPO) was employed for producing a hydrophilic lubricious surface.

2. Method

Materials — Biaxially oriented films of polypropylene (PP) (60 μm in thickness, FOP60; Futamura Kagaku, JAPAN) and poly(ethylene terephthalate) (PET) (2 μm in thickness, H500; Diafoil, JAPAN) were of commercial grade. High density polyethylene (PE) film was prepared by pressing PE pellets (Hi-zex 5305E; Mitsui Petrochemical Industries, JAPAN) at 160 $^{\circ}\text{C}$ to have a thickness of 200 μm . N, N-dimethylacrylamide (DMAA) (Kohjin, JAPAN) was degassed by freeze-thaw cycles under reduced pressure prior to use. BPO was purchased from WAKO Chemical Industries (JAPAN), and was used without further purification.

BPO-treatment — The films were dipped into a 0.1 % BPO solution in toluene for 1 min, then dried at 25 $^{\circ}\text{C}$.

Plasma-initiated Graft Copolymerization — The films, supported by a stainless steel mesh in the reaction vessel, were exposed to argon (Ar) plasma which was excited by a 13.56 MHz radio frequency at a power of 80W. After the treatment of Ar plasma for 15 s at 13 Pa, the pressure in the vessel was immediately reduced to 0.2 Pa, and DMAA vapor was introduced into the vessel to initiate graft copolymerization onto the films. The grafting was carried out for 20 min at a room temperature (24 $\pm$ 1 $^{\circ}\text{C}$) under the DMAA pressure of 1.3×10^2 Pa. The resulting films were washed with methanol using Soxhlet extracting apparatus for 20 h to remove unreacted DMAA and non-grafted PDMAA.

Surface Analysis — DMAA grafted and non-grafted films were investigated by attenuated total reflection Fourier transform infrared spectroscopy (FT-IR-ATR) using DIGILAB FTS40 to determine the surface chemical structures. Surface elemental composition was determined by X-Ray photoelectron spectroscopy (JEOL 90SX).

Measurement of Surface Lubricity — The friction coefficient (μ) of the films were measured by sliding on the surface of PE and PP-g-PDMAA under wet conditions, using the apparatus illustrated in Fig.1(a). Test films ($\phi 10$) were bonded at the end of a load (10g), and one end of the plate was gradually inclined to obtain the initial inclination angle required for the load to begin sliding. The μ value was calculated according to the formula ; $\mu = \tan \theta$. The lubricity of the surface was also evaluated by measuring the frictional resistive force encountered during sliding against a glass surface under water. Test samples ($\phi 16$) were bonded at the end of a load (400g), and the glass was fixed on an inclined plate as shown in Fig.1 (b). The frictional resistive force for the load up and down was measured by a load transducer.

3. Results and Discussion

Graft Copolymerization of DMAA onto Polymeric Films — FT-IR-ATR spectra of DMAA grafted and non-grafted films are shown in Fig. 2. IR absorption due to PDMAA was clearly observed in the spectrum of PDMAA grafted PE (PE-g-PDMAA). In case of PP and PET, the strong absorption at 1630 cm^{-1} , which is attributable to the carbonyl groups in PDMAA, was noticeably appeared. Surface elemental composition of films, measured by XPS are given in table1. PE, PP and PET do not contain nitrogen atom in their chemical structure. Therefore, almost all the

Fig. 2 FT-IR-ATR spectra of DMAA grafted films (lower) and non-grafted films (upper):
(a) PE; (b) PE-g-PDMAA; (c) PP; (d) PP-g-PDMAA; (e) PET; (f) PET-g-PDMAA.

newly produced nitrogen after graft copolymerization are derived from PDMAA at the surface. These data indicate that vapor-phase grafting of DMAA has been successfully achieved. Unlike the procedure where the activated films are immersed into the monomer solution, vapor-phase plasma-graft is simple, rapid and practical.

We have introduced a new modification to the plasma-graft processing, by using BPO as a sensitizer. PDMAA grafted films after BPO treatment contain much more nitrogen atoms compared with untreated films. BPO is decomposed by heat or UV irradiation to produce free radicals which are able to initiate radical polymerization.[9] Therefore, BPO is often used as an initiator of polymerization. Ogiwara *et al.* have reported [10] the vapor-phase photo-induced grafting by using

Table 1 Surface elemental ratio of test films.

	N1s / C1s	O1s / C1s
PP	tr	0.02
PP (Ar plasma)	0.01	0.07
PP-g-PDMAA	0.12	0.18
PP-g-PDMAA (BPO)	0.18	0.20
PE	tr	0.06
PE-g-PDMAA	0.11	0.15
PE-g-PDMAA (BPO)	0.18	0.19
PET	tr	0.38
PET-g-PDMAA	0.12	0.20
PET-g-PDMAA (BPO)	0.18	0.20

BPO as a photosensitizer. In case of the graft copolymerization, free radicals derived from BPO would contribute to extract hydrogen atoms from polymeric substrates to generate polymer radicals which can act as initiators for polymerization and produce graft polymer covalently bound to the underlying surface. The same effect of BPO might contribute to the enrichment of the PDMAA present at the outermost surface.

Surface-lubricity Achievement — The friction coefficient (μ) of test films against PE and PP-g-PDMAA are listed in table 2. The μ values of the PDMAA grafted films against PE surface were significantly reduced, and all the test films exhibited low μ values, below 0.1, against PP-g-PDMAA surface under wet conditions. Indeed, the PDMAA grafted films were felt very lubricious in an aqueous environment when touched with fingers, though non-lubricious in the absence of water.

It is generally recognized that the frictional force between two sliding bodies consists of two components, adhesion and displacement.[11,12] If two opposing surfaces are smooth and non-deformable, the frictional force is dominated by adhesive force which is due to the attractive force between the two surfaces in contact. Bowden and Tabor state most unlubricated polymers, the adhesion term dominates.[13] PDMAA grafted surfaces, which are mostly water in an aqueous environment, form water layer between two opposing surfaces and reduce the adhesive force by eliminating direct solid-solid surface contact.

BPO pretreated films were found to be more lubricious than untreated ones. This result is in good agreement with the nitrogen atom content derived from PDMAA at the outermost surface. The adhesive force is a surface effect, and may be regarded as occurring at the outermost layer. Therefore, surface lubricity would be affected by PDMAA content at the surface.

Fig.1 The methods for determining the coefficient of friction (a) and the frictional resistive force (b).

Table. 2 The coefficient of friction [μ] and the frictional resistive force of test films.

Test films	The coefficient of friction [μ]		Frictional resistive force [N]
	PE	PP-g-PDMAA	
PP	0.16	0.08	2.2
PP (Ar plasma)	0.23	0.09	2.4
PP-g-PDMAA	0.12	0.06	1.4
PP-g-PDMAA (BPO)	0.09	0.06	1.0
PE	0.21	0.09	1.9
PE-g-PDMAA	0.14	0.05	1.6
PE-g-PDMAA (BPO)	0.06	0.06	1.2
PET	0.16	0.05	1.7
PET-g-PDMAA	0.12	0.04	1.5
PET-g-PDMAA (BPO)	0.05	0.04	0.6
PE-g-PDMAA (dry)	0.36	0.65	

The hydrophilic lubricity achieved by coating with hydrophilic polymer while good initially, is often not durable. The hydrophilic polymers readily wear off from the substrate through either leaching or mechanical friction. DMAA grafted films retained low frictional resistive force after sliding the load 10 cycles (Fig. 3), indicating that the PDMAA grafted layer is durable and doesn't easily wear off. Continued rubbing of the surface under water with a moderate finger pressure didn't reduce the lubricity or remove the grafted layer.

Fig. 3 Typical traces of the frictional resistive force measured by a load transducer. The upper trace (a) corresponds to the PET, and the lower (b) to the PET-g-PDMAA(BPO).

5. Conclusion

The approach adapted in this study to prepare biomaterials with desired lubricity is simple, rapid and practical. A hydrophilic lubricious surface has been produced by the vapor-phase plasma-graft of DMAA onto PE, PP and PET films. The modified plasma-graft using BPO as a sensitizer is an effective technique for making the surface more lubricious than the BPO untreated surfaces.

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