Available online at www.sciencedirect.com

ScienceDirect

Thin Solid Films 516 (2008) 6592–6597

thin solid films

www.elsevier.com/locate/tsf

Surface modification of fluorocarbon polymer films for improved adhesion using atmospheric-pressure nonthermal plasma graft-polymerization

Masaaki Okubo [a,*], Mitsuru Tahara [b], Noboru Saeki [c], Toshiaki Yamamoto [d]

[a] Department of Mechanical Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai 599-8531, Japan

[b] Environment and Chemistry Department, Technology Research Institute of Osaka Prefecture, 2-7-1 Ayumino, Izumi, Osaka 594-1157, Japan

[c] Laboratory of Technology Development, Pearl Kogyo Co., Ltd., 3-8-13 Minamikagaya, Suminoe-ku, Osaka 559-0015, Japan

[d] Department of Electrical and Electronic Engineering, Musashi Institute of Technology, 1-28-1 Tamazutsumi, Setagaya-ku, Tokyo 158-8557, Japan

Available online 19 November 2007

Abstract

Flexible thin solid films made of fluorocarbon polymers such as PFA (perfluoroalkoxy fluoroplastics), PTFE (polytetrafluoroethylene), and PCTFE (polychlorotrifluoroethylene) have excellent properties in terms of flexibility, gas and moisture barriers, etc. We develop a surface modification technique for improving the adhesion of the films using an atmospheric-pressure NTP (nonthermal plasma) method followed by graft-polymerization of the hydrophilic monomer. The results of the T-type peeling test show that the peeling strength of the film is thirty times larger than that of the untreated film. It is confirmed from XPS (X-ray photoelectron spectroscopy), FTIR (Fourier transform infrared spectrophotometer) and the SEM (Scanning electron microscope) analyses that a few F atoms exist on the surface and the hydrophilic layer with a thickness is of the order of 1 μm is formed due to the grafting process.

Keywords: NTP (Nonthermal plasma); Thin film; Fluorocarbon polymer; Adhesion improvement; Graft-polymerization

1. Introduction

Flexible thin solid films made of fluorocarbon polymers such as PFA (perfluoroalkoxy fluoroplastics, $-[CF_2-CF_2]_n-[CF_2-CF(OCF_2CF_2CF_3)]_m-$), PTFE (polytetrafluoroethylene, $-[CF_2-CF_2]_n-$), and PCTFE (polychlorotrifluoroethylene, $-[CF_2-CFCl]_n-$) have excellent properties in terms of flexibility, gas and moisture barriers, heat and fire resistances, chemical resistance, electric insulation, etc. Therefore, the applications of these films have been extended to various fields. However, because the molecular structure of fluorocarbon polymers is very stable and the polymers are inactive, it is difficult to adhere the polymers to other substances and to laminate them. If their adhesive property can be improved, applications in electrical devices such as multi-layer flexible electric circuits and flexible organic EL (electro luminescence) displays with a long life are possible because of their higher gas and moisture barrier properties [1].

In order to improve the adhesive properties of such films, liquid-phase etching is often used with the sodium–ammonia submerging method [2,3]. In this method, there are some problems as follows: the processing environment is poor, and a large amount of effluent is drained, which results in a significant environmental load. Further, the surface of the film is chemically damaged by the etching. As a result, not only the excellent optical penetration properties but also the strength of the film are lost considerably.

In the present study, an innovative plasma surface treatment method is proposed for fluorocarbon polymer films. Although low-temperature NTP (nonthermal plasma) technologies improving the surface properties of fibers and polymers have been used for enhancing their adhesion [4,5] and hydrophilicity [6,7], deepening the coloration [8], and shrink-proofing of woollen fabrics [9], the effectiveness is not so significant and does not last for longer time with NTP treatments only. In order to realize the effective and permanent surface treatment, the NTP treatment must be combined with another one such as chemical painting process [7,10]. Based on a similar concept of the

* Corresponding author. Tel./fax: +81 72 254 9230.
E-mail address: mokubo@me.osakafu-u.ac.jp (M. Okubo).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.11.033

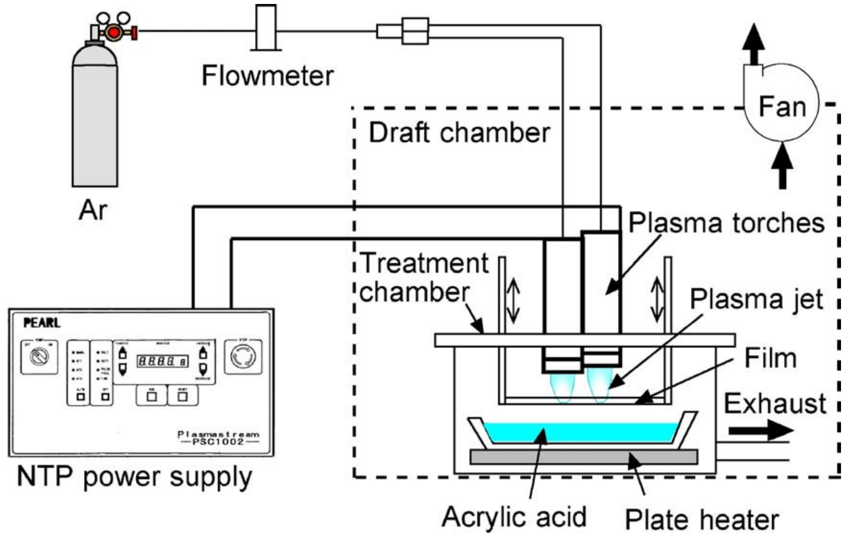

Fig. 1. Layout of experimental setup for atmospheric-pressure NTP graft-polymerization treatment.

combined process, we have developed a new and effective NTP combined surface modification technique for polymer textiles using an atmospheric-pressure NTP method, followed by graft-polymerization [11,12] of the hydrophilic monomer. This process is expressed for fluorocarbon polymer R−F as

$$\text{NTP application:} \quad R - F \rightarrow R\bullet + F\bullet \tag{1}$$

$$\text{Graft} - \text{polymerization: } R\bullet + n(CH_2 = CHCOOH) \rightarrow R{-}[C_2H_3COOH]_n{-} \tag{2}$$

where R is the main chains of C, H, O and F atoms in fluorocarbon polymer, and R• and F• are the radicals.

As compared with the ordinary chemical surface treatment for the films, such as the sodium-ammonia solution submerging method, this is a dry technique and generates a small environmental load. It is confirmed from XPS (X-ray photoelectron spectroscopy) and FTIR (Fourier transform infrared spectrophotometer) analyses that a transparent hydrophilic layer with a thickness of the order of 1 µm is formed on the film surface. The results of the T-type peeling test show that the peeling strength of the film is considerably greater than that of the untreated film. The SEM (Scanning electron microscope) image of the film reveals a very smooth and flat surface.

2. Experimental apparatus and methods

2.1. NTP treatment apparatus and method

Fig. 1 shows the layout of the laboratory experimental setup for the treatment of the films. Industry Ar (purity = 99.99%) is used as the test gas. The fluorocarbon film (thickness = 100 µm, size = 10 × 13 cm) is stretched at the sample holder and NTP jets induced by an atmospheric-pressure Ar corona discharge are applied to the surface. The details of the electric circuit for the plasma jet system are shown in Fig. 2. This system (Plasma

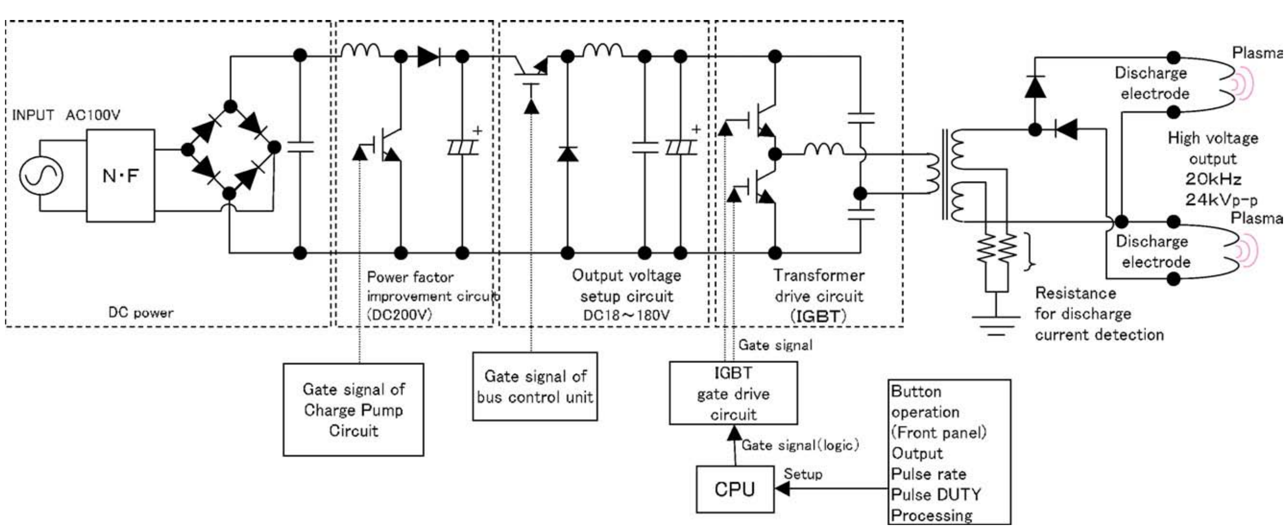

Fig. 2. Electrical circuit of the NTP jet surface treatment system.