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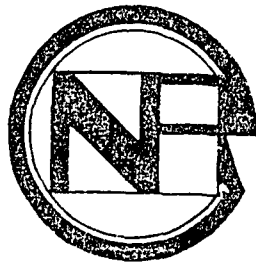
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中国核科技报告

MW 等离子体引发单体在聚四氟乙烯表面接枝共聚

MICROWAVE PLASMA INITIATED GRAFT
COPOLYMERIZATION MODIFICATION OF
MONOMERS ONTO PTFE SURFACE



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MW 等离子体引发单体在 聚四氟乙烯表面接枝共聚

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摘 要

研究了 2.45 GHz 微波非平衡等离子体引发单体在聚四氟乙烯材料表面接枝共聚改性。使用 X 射线光电子能谱 (XPS)、衰减全反射富里叶变换红外光谱 (ATR-FTIR) 及扫描电子显微镜 (SEM) 和湿法技术对原始样品及接枝后的样品进行了测试分析。结果表明, 接枝后聚四氟乙烯表面的化学结构、成分和形貌均发生了相当大变化, 出现了明显的脱氟交联, 表面上引入了不同种类和不同含量的含氧功能基团。对样品进行的润湿实验和粘接实验证明, 接枝样品表面的亲水性极佳, 粘接性也得到了明显改善。分析和实验结果都证实了接枝已获成功。

MICROWAVE PLASMA INITIATED GRAFT COPOLYMERIZATION MODIFICATION OF MONOMERS ONTO PTFE SURFACE

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ABSTRACT

A graft copolymerization modification technique of monomers onto polytetrafluoroethylene (PTFE) surface initiated by a 2.45 GHz non-equilibrium microwave plasma has been investigated. Standard X-Ray Photoelectron Spectroscopy (XPS), Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR), Scanning Electron Microscopy (SEM) and wetting techniques were used for examination and analysis of samples. Considerable changes in chemical structure, composition and in morphology of grafted surface of PTFE were found. Results showed the occurrence of noticeable defluorination and cross-linked structure on grafted surface, and indicated that different kinds and contents of oxygen-containing functional groups were introduced into the surface of PTFE. Wetting and adhesion experiment of the sample proved that significant improvements in hydrophilicity and adhesion of surface were exhibited. These results confirmed the success of grafting.

INTRODUCTION

Polymers such as polytetrafluoroethylene, polyethylene, polypropylene, polystyrene, polyurethanes, etc. are widely used in the home, industries, and high-science-technology fields for their excellent properties. However, the expanding area of applications is limited by their very poor adhesion caused by a nonpolar structure on surface, leading to poor bonding properties. These polymers could be used even more extensively if they had enhanced hydrophilicity and adhesion. Consequently, various processes by surface modification have been developed to the tailoring of these properties. Among them, grafting based on low temperature plasma technology has become an international growing interesting topic owing to its attractive advantages compared with conventional methods, and especially non-equilibrium microwave plasma has gained attention in processing of materials due to the promotion of various reactions along with reducing the temperature needed in traditional chemical reaction, etc. under the joint effects of plasma physics, plasma chemistry and photochemical processes^[1], leading to the benefits in " low-temperature, low-pressure, high rate, contamination free, lower-damage processing.

In this paper, we report some results from the investigation of graft copolymerization modification of PTFE surface with kind of one or another reactive monomers using non-equilibrium microwave plasma at 2.45 GHz under various operating conditions. The goal of this work is to improve the hydrophilicity and adhesion of PTFE without changing its good bulk properties in applications such as metal-polymer, polymer-polymer or polymer-adhesive interfaces.

1 EXPERIMENTAL

The graft copolymerization was carried out in a microwave plasma enhanced CVD experimental apparatus as shown schematically in Fig. 1.

Commercial products of PTFE (typical molecular structure: $[-CF_2-CF_2-]_n$) and monomers were used. Prior to treatment, all samples were washed thoroughly with acetone, alcohol and distilled water and then dried in air, and subsequently in vacua. A sample to be treated was placed on a substrate holder, which is immersed in plasma for most cases. Different type of feed gas of high purity (Ar, N₂, O₂, H₂) or their mixture were employed, respectively. Selected monomers with unsaturated double-bonds like acrylic acid, etc. were reagent grade. Additional vaporization procedures for liquid monomers were used to feed them into the plasma reactor.

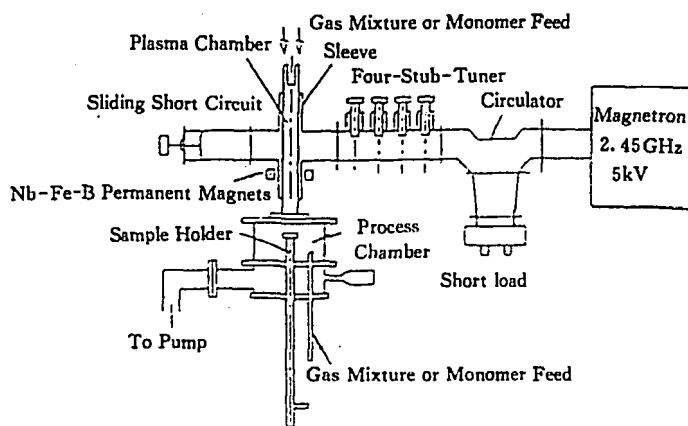


Fig.1 Schematic diagram of experimental apparatus for graft copolymerization using microwave plasma

Processing gases and monomers were introduced into vacuum chamber via a three channel inlet system equipped with mass flow controller and needle valves, respectively. The base pressure of the system was below 10^{-2} Pa. The experiments of graft copolymerization modification were conducted using a two-stage combination process involving initial irradiation pretreatment using microwave plasma of processing gases only, and subsequent graft copolymerization in plasma of monomers-processing gas mixture. The appropriate operating condition such as gas flow rates, gas composition, pressure, microwave power and sample position in plasma, type and concentration of monomers, and duration of plasma pretreatment and plasma graft were experimentally selected under which the graft copolymerization was reached successfully.

2 RESULT AND DISCUSSION

2.1 XPS Spectra Analysis

The chemical changes of polymer surface was investigated with XPS (X-Ray Photoelectron Spectroscopy) as described by Clark and Shuttleworth^[2]. Fig. 2 shows the typical XPS survey scan spectra of a clean untreated (a) and a grafted (b) PTFE samples. A very strong peak at 690 eV corresponding to F1s and a C1s peak at 285 eV was clearly seen, and a very weak oxygen (O1s) signal was observed from Fig. 2 (a). After grafting (b), fluorine (F1s) signal was remarkably decreased and became barely observable, indicating the occurrence of defluorination

due to scission of F—C bonds and the release of F and F—C fragments. In addition, the spectra displays a significant increase in the amount of oxygen (545 eV), and a small amount of nitrogen was also measured (approximately 2%).

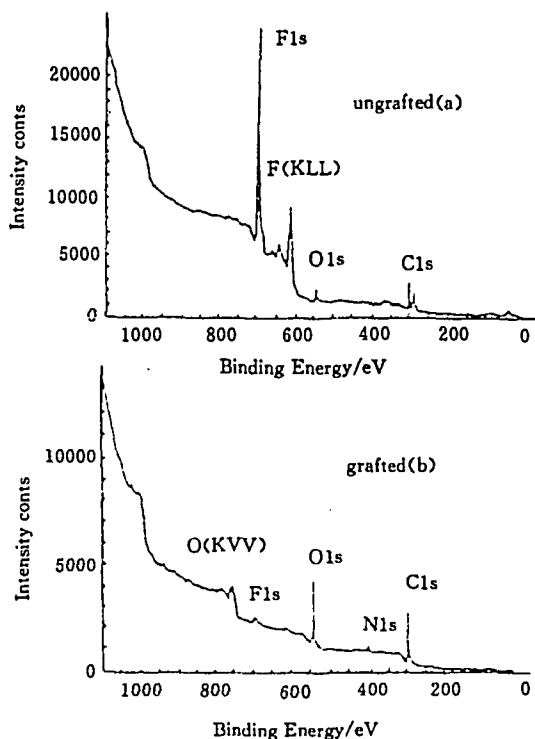


Fig. 2 The typical XPS survey scan spectra of clean untreated (a) and grafted (b) PTFE samples

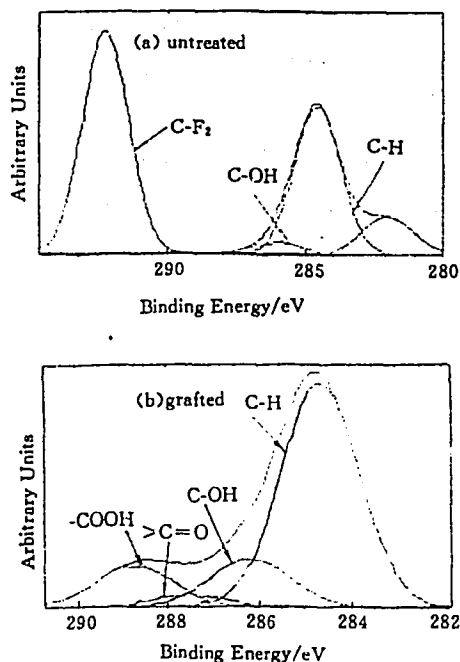


Fig. 3 XPS high resolution C1s spectra for clean untreated (a) and grafted (b) samples of PTFE

Fig. 3 gives the high resolution XPS spectra of C1s for both untreated and grafted PTFE samples. The appearance of an extra shoulder towards higher binding energy side of the C1s peak can be ascribed to the presence of different oxygen-containing functionalities such as hydroxyl (—OH), carbonyl (>C=O) and carboxyl (—COOH) on grafted surface, respectively. The corresponding elemental composition calculated from XPS data is listed in Table 1.

Table 1 Results of the XPS analysis:

Atomic composition of grafted sample and untreated sample

Species	Atomic Composition/%					
	C1s	F1s	O1s	N1s	F1s/C1s	O1s/F1s
Untreated	46.47	49.79	3.74		1.071	0.075
Grafted	69.83	1.53	26.51	2.13	0.022	17.327

We noted that the F1s/C1s ratio decreased from 1.071 (untreated) to 0.022 (grafted) and O1s/F1s ratio increased from 0.075 (untreated) to 17.327 (grafted), confirming the occurrence of noticeable defluorination and incorporation of a large amount of oxygen-containing polar functional groups into the grafted surface of PTFE by graft copolymerization.

2.2 Analysis of ATR-FTIR Spectra

ATR-FTIR (Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy) spectra of grafted and ungrafted samples of PTFE were obtained over a range of $(400 \sim 4000) \text{ cm}^{-1}$, which allowed to get a separate identification of the chemical groups. The typical ATR-FTIR spectra are shown in Fig. 4, and only those main peaks are labeled

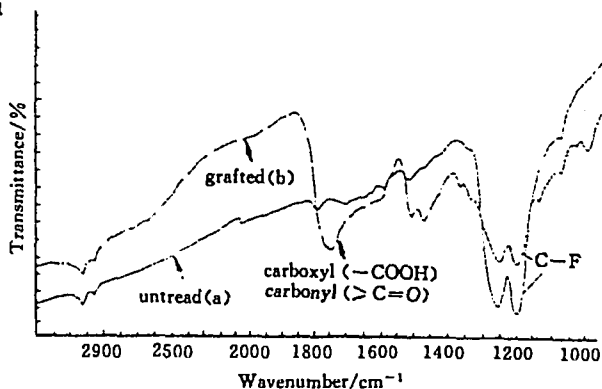


Fig. 4 The typical ATR-FTIR spectra of ungrafted (a) and grafted (b) samples

which are relevant to our discussion. The spectrum of untreated surface indicated a strong characteristic absorption peaks at wave numbers of 1205 and 1145 cm^{-1} , corresponding to the absorption of F—C bond stretch vibration. In comparison between spectra of two samples, an obvious decrease in absorption intensities (C—F bond stretch vibration) located near the same wave numbers on grafted sample was observed and the spectrum showed relatively broad peaks due to defluorination and cross-linking. Specially, the new absorption peaks at a broad band in the range of $(1550 \sim 1750) \text{ cm}^{-1}$ for grafted sample appeared and can be attributed to the introduction of oxygen-containing polar functionalities onto surface, which will be assigned to the carboxyl ($-\text{COOH}$) and carbonyl ($>\text{C}=\text{O}$) groups^[3,4]. This proved the occurrence of grafting and further supported the XPS data.

2.3 Morphological Observation by SEM

Both untreated and grafted samples were examined by SEM (Scanning Electron Microscopy). Fig. 5 gives the typical SEM photographs of surface morphology of (a) untreated and (b) grafted samples. Fig. 6 is the micrograph of the cross section of graft sample and Fig. 7 is its magnifying micrograph with high resolution. From Fig. 5, the formation of rough structure on grafted surface was clearly observed in comparison with the untreated sample, which probably connecting with an

irregular aggregation of dispersed microglobule, grain, and nodules caused by grafted branches and small holes formed by oxygen-rich species chemical etching. Fibriform heterostructure layer was also formed, showing different structural feature compared to the bulk material (Fig. 6 and Fig. 7), which further confirmed the success of graft.

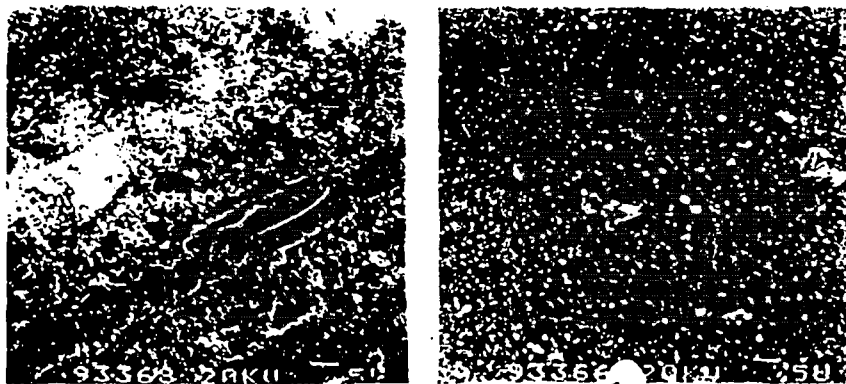


Fig. 5 Typical SEM photographs of surface morphology of (a) untreated and (b) grafted samples

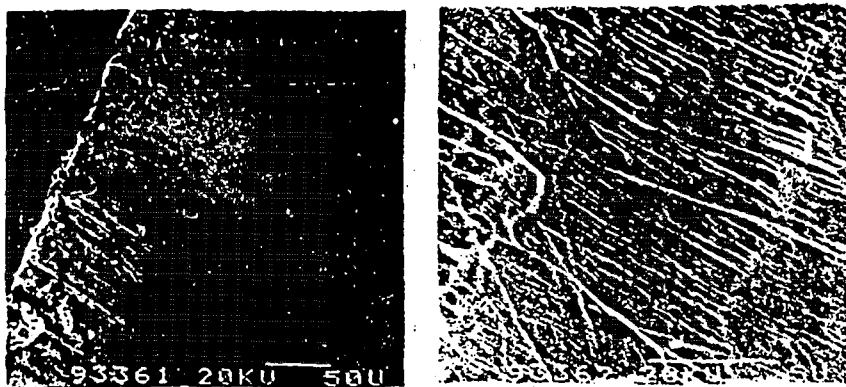


Fig. 6 The SEM micrograph of the cross section of graft sample

Fig. 7 Magnifying micrograph with high resolution from Fig. 6

2.4 Improvement in Hydrophilicity

The most widespread way for determining the energetic characteristics of a solid surface is measuring the equilibrium contact angle between the solid and wetting liquid^[5,6]. Simple tests of contact angle with both running water and double-distilled water were used to examine the differences in surface wettability (hydrophilicity here) caused by graft copolymerization using microwave plasma in this work. Washing samples with water, the water spread rapidly on entire grafted side of sample exhibiting a near zero value of contact angle (109° for original PTFE^[7]),

indicating an excellent hydrophilicity. The hydrophilicity for unexposed part to plasma of PTFE is unchanged and shown a behavior similar to the untreated one, and only a ball-like drop of water on it was observed. It is evident that the modification of surface has been reached without modifying the bulk properties. Enhanced hydrophilicity might be caused by the presence of polar groups due to surface oxidation or the rough structure produced by plasma pretreatment and graft copolymerization. Normally, at higher values of O1s/F1s ratio featured by the incorporation of more oxygen-containing groups onto surface and the release of more fluorine from it, lowering of the contact angle is expected. This leads to the enhancement of surface energy and, therefore, better wetting.

In addition, reproducible results on wetting of PTFE can be obtained for all samples after a long period in storage, whereas the hydrophilic effect of other process like corona discharge treatment, etc. disappears within a limited period.

2.5 Improvement in Adhesion

A set of adhesive experiments between PTFE and metal aluminium with epoxy resins adhesive were carried out for estimating the improvement in adhesion after graft. Excellent adhesive strength between the graft sample and aluminium was obtained compared with peel strength of untreated sample. The adhesive improvement is believed not only due to the surface cleaning by plasma and the formation of rough structure produced by the plasma treatment^[8], which brings about the increases in adhesive surface area and the mechanical bite force between two surfaces to be adhered via adhesive (playing a role of naillike), but also arise from the incorporation of oxygen-containing functionalities into the polymer chains increasing the polarity of PTFE and change of adhesion concerning surface free energy. Of course, the elimination of weak boundary layers (WBL) and the formation of cross-linked structure will also help the increase of adhesive bond strength of polymer.

3 SUMMARY

We demonstrated that a two-stage combination processing technique using microwave plasma can be utilized for surface modification of PTFE by grafting of selected monomers under appropriate operating parameters in suitable processing gases. Considerable changes in chemical structure, composition and physical morphology of surface were found from different surface analyses on samples after graft, which probably caused by chemical etching, grafting reaction occurring via chain scission and chain transfer and the combination between different free radicals and

surface dangling bonds formed in plasma. Strong evidence was found that the formation of rough structure on grafted surface, the occurrence of noticeable defluorination and cross-linked structure on grafted surface, and different polar oxygen-containing functional group incorporation onto the polymer surface by grafting are largely responsible for the significant improvement in hydrophilicity and adhesion of PTFE.

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