

PLASMA-INDUCED GRAFT POLYMERIZATION OF ACRYLIC ACID ONTO POLY(ETHYLENE TEREPHTHALATE) FILMS: HYDROPHILIC MODIFICATION

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ABSTRACT. A complete and permanent hydrophilic modification of poly (ethyleneterephthalate) (PET) films is achieved by argon-plasma irradiation, subsequently grafting acrylic acid (AA) in vapor phase onto their surface. Both Ar plasma irradiation alone and post grafting AA rendered a complete hydrophilicity to PET surfaces. However, the hydrophilicity of the PET surface, only treated with the Ar plasma, is not permanent. In contrast, PET films, irradiated by the Ar plasma, exposed to air, and subsequently grafted with AA monomer, are permanently hydrophilic. Degradation of polymer chains on the plasma-irradiated surface is proportional to time of exposure. Electron spectroscopy for chemical analysis (ESCA) confirmed the grafting of AA onto the film surface, which results in a large amount of incorporated oxygen-containing functional groups like carboxylic ($O - C = O$) and carbonyl ($C = O$). The morphology of grafted surfaces, observed by scanning electron microscopy (SEM), displays some large area of microporosity compared to relative smooth morphology of the control one. Grafted functional groups and surface microporous structure are the main factors to enhance hydrophilicity of the PET films. **Keywords:** *Plasma-induced graft polymerization, polymer degradation, oxygen-containing functional groups, hydrophilicity, microporosity and electron spectroscopy for chemical analysis (ESCA).*

1. Introduction

Polymeric materials hold considerable interest in the field of biomaterials for scientists in recent years. Tissue engineering culture, minimizing protein adsorption to prevent membrane-fouling for protein ultrafiltration, immobilization of biologically active molecules and living cells, etc., are rather closely related to hydrophilic characters of polymer surfaces [1-3]. Surface hydrophilicity of the polymer can be achieved by the incorporation of oxygen-containing functional groups, such as $-COOH$ and $-OH$, which are usually not coupled with molecular chains of the polymer surface. Surface modifications could enhance mechanical interlocking, and create functional groups, improving wetting and/or chemical bonding of a polymer surface. Synthetic polymers, therefore, often require selective modifications to introduce specific functional groups onto surfaces for proper purposes, ex. binding of biomolecular, gas barrier, etc.

The conventional methods (wet chemistry) for the hydrophilic modification of polymer surfaces have been performed by various chemical treatments, usually accompanied by damaging polymer bulk, hence affecting its properties. In contrast to

the wet chemistry, the polymer surface, exposed to plasma, can be modified to enhance its hydrophilicity, compatibility and biofunctionality. Moreover, the modified surface is, in general, confined to a top-surface layer less than *several hundred nanometers* through polymer thickness. Therefore, desirable properties of bulk layers are usually maintained. However, on most polymer surfaces, the gained hydrophilicity is usually not permanent, and disappears or diminishes significantly after only plasma irradiation. The irradiated surface gradually restores its hydrophobicity due to fragmented low-polymer chains on surface layers, tending to reorient into bulk layers. This resulted in decrease in a number of functional groups, thereby decreasing its hydrophilicity. Post-graft copolymerization can fix radicals by grafting a hydrophilic monomer onto the irradiated surface, therefore, raising the lifetime of surface hydrophilicity. In addition, the grafting of a specific monomer makes a surface modified with suitable chemical functionality for biomaterial applications [4-7].

In previous paper [8], hydrophilic improvement of PET fibers in moisture absorption and dyeing performance has been reported. Absorption enhancement are due to the existence of carboxyl groups: $O - C = O$, incorporated on to PET fiber surfaces, furthermore, the conditions of the plasma irradiation as well as graft-polymerization have considerably effects on the hydrophilic durability of PET fibers.

This paper describes PET films, irradiated with a mixture of inert gases like helium/argon (He/Ar) at pressure of one-atmosphere, then subsequently graft-polymerized with acrylic acid in vapor to enhance their hydrophilic durability over time. Effects of irradiation time on a weigh loss ratio and grafting degree of PET's films were investigated. Oxygen-containing functional groups, characterized by electron spectroscopy for chemical analysis (ESCA), were used to roughly estimate hydrophilic capability of the grafted surface. Surface morphology of the grafted surface was observed by scanning electron microscopy (SEM). Influence of the grafted functional groups and surface morphology upon surface hydrophilicity will be discussed.

2. Experimental Procedures

2.1. Sample preparation

In PET film structure, two groups of $O - C = O$ bond, symmetrically-bonded to an aromatic ring, seem to be stable. Besides, there are $-CH_2 - CH_2$ bonds with lower bonding energy. Hence, the degradation of molecular chains on its surface might occur at $C - H$ and $C - C$ molecular bonds when the

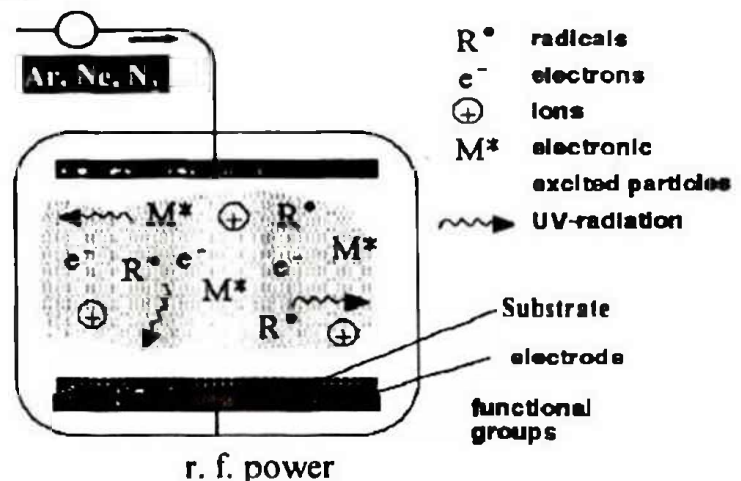


Fig.1. Principle of plasma reaction inside electrodes

molecular chain absorbs plasma-energy from activated species and ultraviolet rays during the plasma irradiation. The principle of plasma reaction occurring between two electrodes is described in figure 1. Glow discharge plasma at one-atmosphere was generated in a plasma reactor (manufactured by Pearl Kogyo Co. Ltd, Osaka, Japan) coupled with parallel plate electrodes, which were covered by dielectric barrier-ceramic, and operating at radio frequency of 13.56 MHz. A PET film sample of 0.2 mm in thickness, provided by Asahi Glass Fibers Co. Ltd. (Japan), was placed between two electrodes, and then irradiated with the mixture of He/ Ar inert gases, introduced by the constant flow rate of 850ml /150ml min⁻¹ (STP), and introduced into a plasma chamber. Irradiated from 10 sec to 3 min, with plasma power-density of 1.75 W/cm², at electrode surface temperature of about 70^oC - 80^oC, each sample was removed from the plasma chamber, then immediately weighted to estimate degradation state of surface-layers. The irradiated sample was then grafted with acrylic acid (AA) of 99.5% conc. in a glass tube evacuated to 133 Pa at two level of constant temperature: 60^oC as well as 70^oC; the grafting process lasted for 8 hours and 1 hour, respectively. Taken from the glass tube, the sample was extracted by hot methanol in a Soxhlet extractor for 2 hours to remove unreacted remaining monomer and homopolymers.

2.2. ESCA characterization of modified surface

ESCA measurement was performed on a Kratos ESCA-3300 spectrometer, employing MgK α (1253.6 eV) X-ray source. The electron take-off angle was adjusted around 60^oC with respect to the film surface. The pressure in the analysis chamber was maintained at about 10⁻⁵ Pa during the data acquisition. The X-ray source was run at the anode voltage of 8 kV and current of 30 mA.

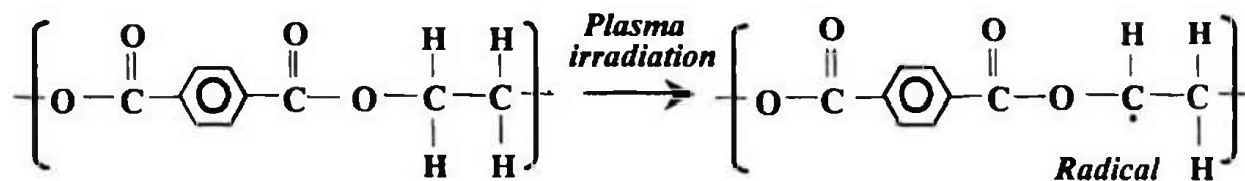
2.3. Surface morphology observed by SEM

Surface morphology of the grafted films was observed by a scanning electron microscope (SEM), model JEOL JSM-5200. For better electric conductivity, a sample's surface was coated with thin gold layer before the examination. The observation was performed to determine the quality of polymer depositions, and especially to check whether micropores appear on the grafted surface.

3. Results and Discussion

3.1 Degradation of plasma-irradiated surface

The degradation of the film surface irradiated by plasma seems to be predominant effects of the discharge interaction between its surface and activated species like ions, particles, etc. This process led to an almost complete breakdown of C — H or C — C bonds, producing carbon radicals on irradiated surfaces. The polymer degradation can be described as follows:



Where: C[•] is a radical grown by the degradation of a molecular chain on the PET surface. The polymer degradation, characterized by weight-loss ratio, was calculated in the following expression:

$$W_L (\%) = -100 * (W_1 - W_0) / W_0 \quad (1)$$

Where: $W_L (\%)$ is the weight-loss ratio; W_0 and W_1 are the weight of a sample before and after the GDP treatment. The minus mark is denoted as the weight loss of the molecular chains due to the degradation.

The degradation of the molecular chains on the irradiated surface layers versus the time of exposure is indicated in the Fig. 2. It is clearly that the weight loss ratio, indicating the level of the degradation, went up with further exposure time. Large dispersion of the weight loss is ascribed to the effect of the density of activated species, which collided with the film surface as well as the cross-linking of radicals generated on the PET surface during the plasma irradiation. The similar results have also been found in the report of Yasuda *et. al.*[9]. Exposed to air, these radicals were reacted with oxygen in air to produce peroxides and (–COOH) hydroperoxides. These peroxides, being initiators for the subsequent graft polymerization were formed as following reactions:

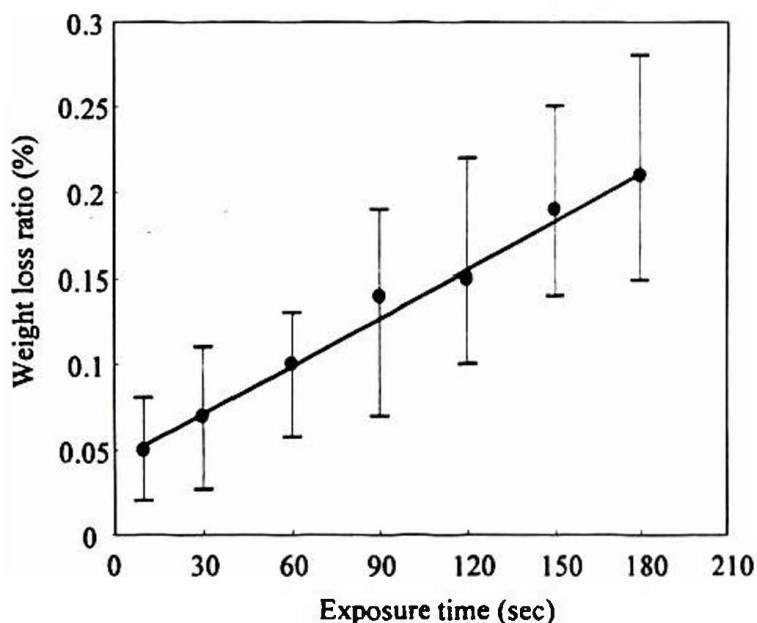
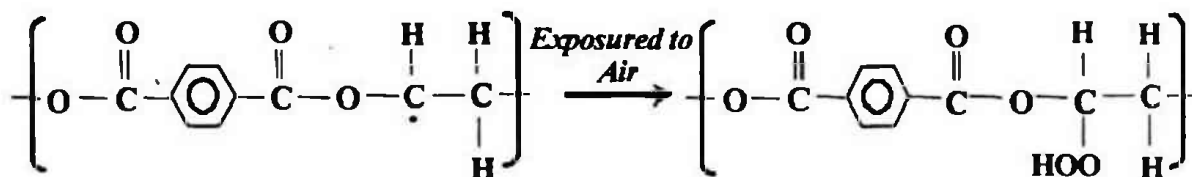
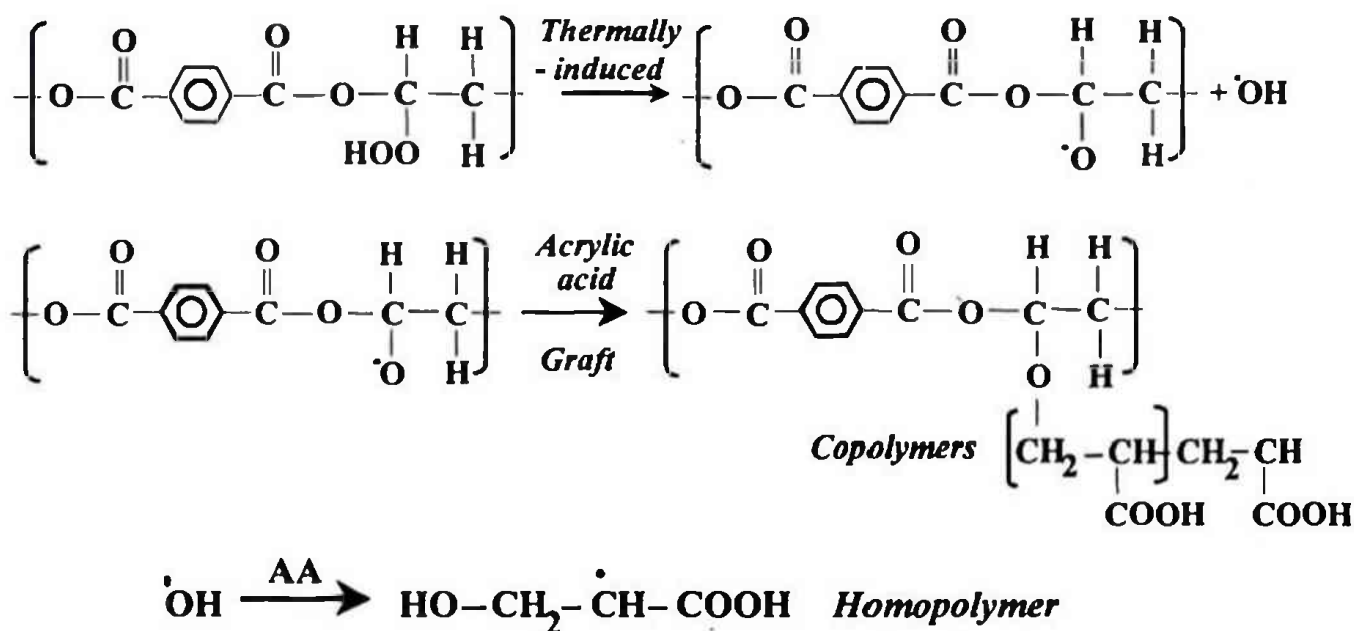


Fig. 2. Degradation of polymer surface versus the time of irradiation

3.2 Effects of the exposure time on grafting degree

Owing to thermally-induced degradation coincident with the presence of the AA monomer in vapor, CO[•] and [•]OH radicals, decomposed from the hydroperoxides, were then graft-polymerized in a glass tube, evacuated to 133 Pa at temperature of 60°C for 8 hrs as well as 70°C for 1 hr. Grafted with the AA monomer of 99.5% conc., these CO[•] radicals, initially serving as activate sites, reacted with the monomer to create copolymers while [•]OH radicals, also reacted with the same monomer, were changed into homopolymers.



The wettability of the grafted sample, reflected by grafting degree, was calculated as follows:

$$G (\%) = 100 * (W_2 - W_1) / W_1 \quad (2)$$

Where: W₁ and W₂ are the sample's weight measured before and after the graft polymerization, respectively.

Fig. 3 shows the grafting degree of the graft polymerized PET film surface as a function of the exposure time at different grafting temperatures. The highest grafting degree was achieved at

30-sec of the exposure time. With further plasma irradiation, the grafting degree gradually went down, then leveled off at

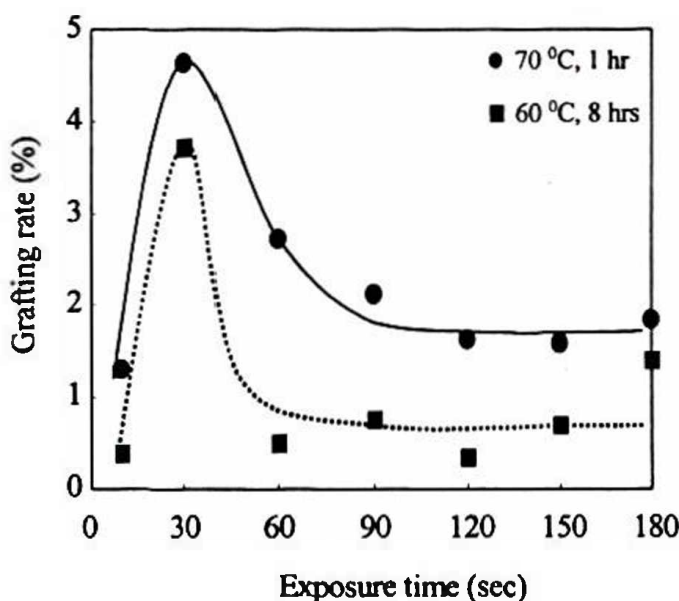


Fig. 3. Relationship between the grafting degree & exposure time of the PET film surface

over 90-sec. Hence, the longer irradiation time than 30-sec might cause unfavorable etching, cross-linking and degradation of the PET surface, which resulted in a no net gain of active species on the irradiated surface for subsequent graft-polymerized process.

Although the polymerization time diminished to 1 hour, the higher grafting degree coincident with the higher amount of homopolymers was gained at grafting temperature of 70°C. This can be assigned to a large number of decomposed radicals, CO \cdot and \cdot OH, owing to the thermally induced degradation, reacted with the AA monomer. The same tendency of the grafting degree versus the time of exposure has also been reported by Choi *et. al.* [10].

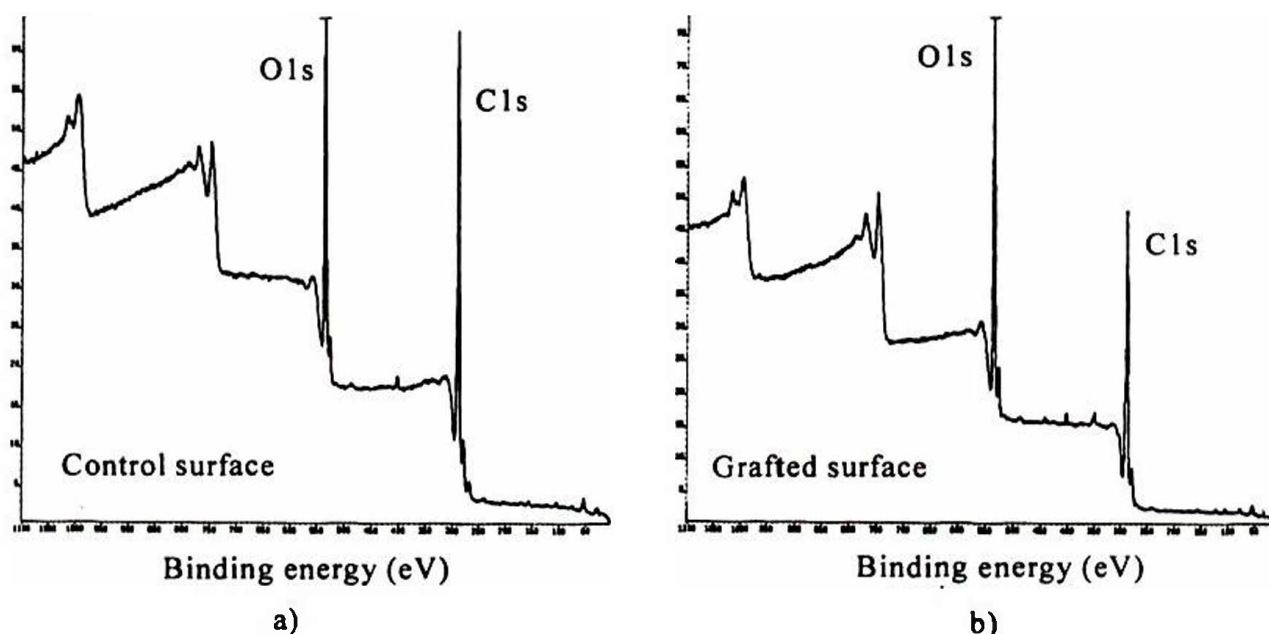


Fig. 4. Wide-scan spectra of a) the control surface & b) the surface irradiated for 30-sec, subsequently grafted at 70°C for 1 hour

3.3. ESCA characterization

The chemical compositions of the PET film surface were analyzed by an ESCA technique. Figure 4 shows wide-scan spectra of a) the control and b) the surface irradiated for 30-sec subsequently grafted at 70°C for 1 hour. Peaks of carbon and oxygen binding energies are located at 285 eV and 532 eV, respectively. It is noteworthy that the relative surface-atomic concentrations

Treatment	Surface chemical compositions, %		
	C _{1s}	O _{1s}	O _{1s} /C _{1s}
Untreated	73.1	26.9	36.7
Grafted	67.3	32.7	48.6

Table 1. Atomic compositions on the surface irradiated for 30-sec and subsequently grafted at 70°C for 1 hour

of oxygen and carbon were significantly altered: the C1s peak of the grafted surface is lower than that of the control one while O1s peak of the grafted surface is little higher than that of the control surface (Fig. 4 & Tab. 1). Moreover, the O_{1s}/C_{1s} ratio, shown in table 1, went up from 36.7 % to 48.6 % for the control and grafted surface, respectively. Furthermore the oxygen content rose from 26.9% to 32.7% corresponding to the control and grafted surface, respectively. The considerable increase in oxygen atoms (O_{1s}) is assigned to a large amount of oxygen-containing groups incorporated onto PET grafted surface. Figure 5 shows high resolution scans of the C_{1s} core-level spectra for the surface, irradiated for 30-sec subsequently graft-polymerized at 70°C for 1 hour and the control one.

Line-shape analysis by the deconvolution indicates that the C_{1s} spectrum of the control surface is composed of three distinct peaks at binding energy (BE) of 285.0, 286.5 and 289.1 eV, assigned to the $C^* - H$, $C^* - O$ (e.g., ether, ester) and $O - C^* = O$ (e.g., carboxylic acid, ester) groups, related to an aromatic ring $C_6H_4 -$, $CH_2 - CH_2 - O$ and $CO - O$ groups, respectively. These assignments are also in good agreement with the structure of a PET repeating unit:

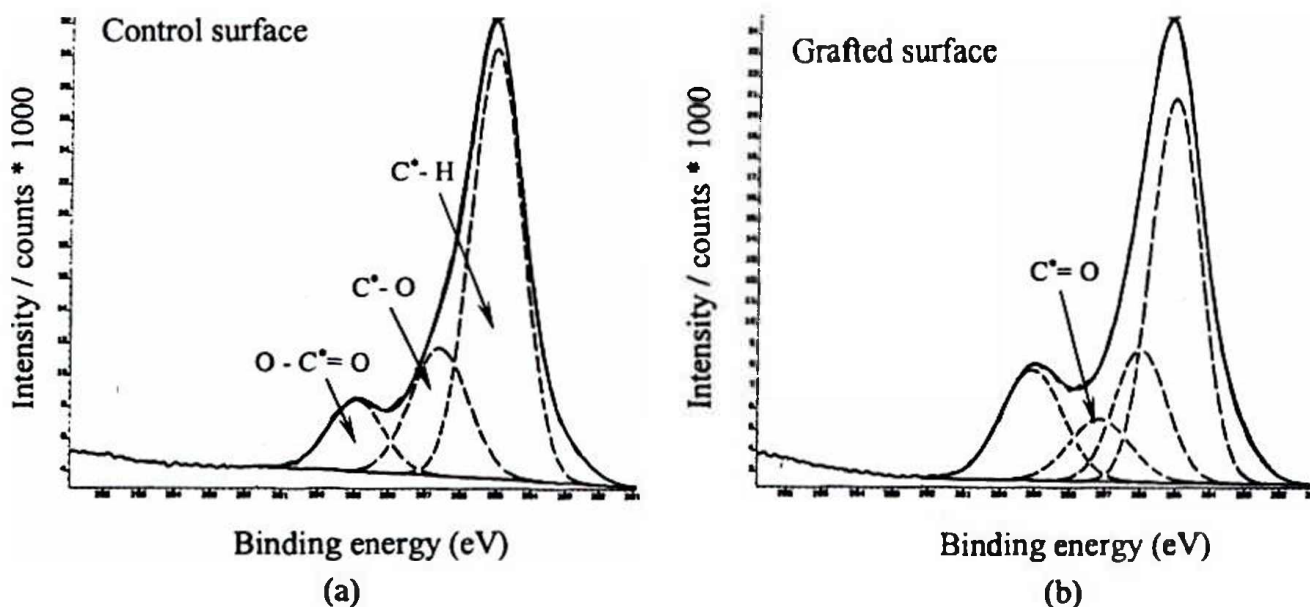


Fig.5. Line-shape & high-resolution analysis of the C_{1s} peak spectra for (a) the control surface and (b) the surface irradiated for 30-sec subsequently grafted at 70°C for 1 hour

The relative chemical compositions of C_{1s} spectra on the grafted surface are shown in table 2. There is a relative increase in the content of $O - C^* = O$ carboxyl groups from 11.6 to 16.9% and the $C^* = O$ carbonyl group is 9.4 % while the content of $C^* - H$ linkage in the aromatic ring and $C^* - O$ groups decreased from 67.5 to 56.6 % and from 20.9 to 17.1 %, respectively. These data suggest that the graft-polymerization mainly involves in the modification of $-C_6H_4-$ and $-CO-$ groups.

Moreover, post-plasma reaction in air of free radicals, generated by broken molecular chains and dehydrogenation mechanisms, led to the formation of carbonyl functional groups: $C^* = O$ at 287.9 eV, a new linkage from the $C^* - O$ group created by oxidation processes. Clearly, the PET surface was oxidized due to a large amount of oxygen-containing functional groups incorporated onto the PET film surface. These functional groups increase hydrogen bonding force and the surface free energy of the film surface. Hence, hydrophilicity of the grafted PET surface was considerably enhanced.

3.4. Morphologies of PET film surface

Figure 6 shows surface morphologies of the control and grafted surfaces. The

control surface (Fig. 6, left) looks like smooth while the modified one (Fig. 6, right) seems to be rough with regular corn-structure. The morphological distinction is attributed to the fragmentation of polymer chains caused by the surface etching, and to grafting AA monomer onto the radicals, decomposed from the hydroperoxides. It is assumed that the roughed surface is one of main factors that enhance hydrophilicity of the PET surface.

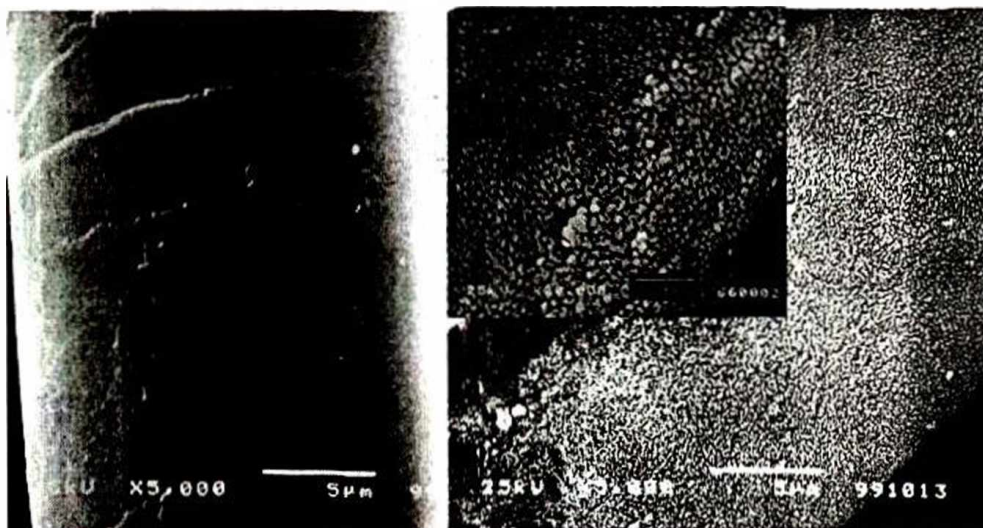


Fig.6. SEM micrographs of the film surface irradiated for 30-sec subsequently grafted at 70°C for 1 hour, (left) the control surface, and (right) the grafted one

4. Conclusions

Plasma-induced graft-polymerization of acrylic acid onto the poly(ethylene terephthalate) (PET) film surface significantly improved its hydrophilicity. The PET surface, irradiated for 30-sec and subsequently grafted with the AA monomer at 70°C, shows the highest grafting degree. The characterization of the grafted surface clearly

Decomposition of the C_{1s} peak				
C_{1s} component, %				
Treatment	C^*-H	C^*-O	$O-C^*=O$	$C^*=O$
Untreated	67.5	20.9	11.6	
Grafted	56.6	17.1	16.9	9.4

Table 2. Relative chemical compositions of C_{1s} spectra on the surface irradiated for 30-sec subsequently grafted at 70°C for 1 hour

confirmed the large amount of oxygen-containing functional groups were incorporated onto the PET film in the form of $O - C^* = O$ and $C^* = O$, being the clear indication of the hydrophilic surface. Shown by SEM micrographs, film surfaces, grafted by copolymers, show their surface morphology like the regular corn-surface that is clear evidence in microporous structure. This suggests that hydrophilic enhancement is closely related to oxygen-functional groups incorporated onto the PET surface and its microporous morphology.

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TRÙNG HỢP & CÂY GHÉP AXÍT ACRYLIC VÀO BỀ MẶT PHIM POLY(ETHYLENE TEREPHTHALATE) BẰNG PLASMA: BIẾN TÍNH THẨM ƯỚT

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Biến tính thấm ướt của *poly(ethyleneterephthalate)* (PET) phim, ổn định theo thời gian, có thể được thực hiện bằng phương pháp chiếu xạ khí argon-plasma, và trùng hợp ghép với hơi axít acrylic (AA). Cả hai phương pháp chiếu xạ plasma và trùng hợp ghép AA monome đều tăng khả năng thấm ướt của bề mặt PET phim. Tuy nhiên nếu xử lý bề mặt PET bằng các phương pháp trên nhưng riêng rẽ, thì tính thấm ướt của PET phim bị suy giảm theo thời gian. Trong khi đó kết hợp cả hai phương pháp xử lý trên sẽ cho phép PET phim duy trì tính thấm ướt theo thời gian. Kết quả nghiên cứu đã chỉ ra rằng sự phân rã của các chuỗi phân tử lớp bề mặt polyme tỷ lệ thuận với thời gian chiếu xạ. Phổ ESCA đã cho thấy sự ghép-trùng hợp của AA monome đã cho một số lượng lớn các nhóm chức như: (O – C* = O) carboxylic & (C* = O) carbonyl, được cây ghép vào bề mặt PET phim. Hình thái bề mặt của bề mặt PET phim được xử lý là màng copolyme có độ dày vài trăm nanomet, có đặc tính thấm ướt, có cấu trúc lỗ xốp và liên kết hoá học với lớp PET nền. Điều đó có thể quan sát bằng kính hiển vi điện tử quét (SEM). Ghép-trùng hợp các nhóm chức và cấu trúc lỗ xốp của bề mặt phim sau khi xử lý là những nhân tố chính để tăng khả năng thấm ướt của PET phim.

Từ khoá: Trùng hợp ghép bằng chiếu xạ plasma, đứt mạch chuỗi polyme, nhóm chức, tính thấm ướt, vi lỗ & phổ tia X cho phân tích hoá học (ESCA).