

# Surface Modification of PTFE by $^{60}\text{Co}$ $\gamma$ -Ray Irradiation

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**ABSTRACT:** Surface carboxyl groups were formed during the  $^{60}\text{Co}$   $\gamma$ -ray irradiation of poly(tetrafluoroethylene) (PTFE) in air. Fourier transform infrared spectroscopy enables the detection of surface carboxyl groups. The contact angles were used to calculate the dispersive and polar components of the surface free energy according to a two-liquid method. The  $\gamma$ -ray irradiation of PTFE mainly caused degradation of the polymer. The concentration of carboxyl groups, the wettability, the friction, and the dispersive and polar components of the surface energy and the crystallinity on PTFE surface were increased, while the particle size of PTFE decreased with increasing irradiation dose. A highly modified PTFE was used to reduce the aqueous liquid repellent properties of PTFE. A 20 kGy dose for modified PTFE surface was suitable in air additivity in antifriction, anticorrosion, antifouling, lubrication, and noise reduction coatings. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 435–441, 1998

**Key words:** PTFE; surface modification;  $^{60}\text{Co}$   $\gamma$ -ray irradiation

## INTRODUCTION

With a high dissociation energy of C—F bond, poly(tetrafluoroethylene) (PTFE) displays a high thermal stability, a high chemical resistance, a low friction coefficient, and a low surface energy. These properties, which are very important for some specific applications, together with the rubbing action, cause considerable disadvantages in applications in which adhesion-related problems are concerned. Nearly 3 decades ago, Zisman observed the difficulty in wetting PTFE, as indicated by the high contact angle for a series of liquids on it. He subsequently determined the critical surface tension of wetting for Teflon and later demonstrated that the fluorine atoms were responsible for the low surface energy. Since the materials with low surface energy can be used to prepare promising high-quality protective coatings, fluorocarbon in the molecular structure are characterized by several excellent properties. It is possible to use the polymers that

contain fluorocarbon groups in the molecular structure to produce a surface to which some organisms could not adhere with tenacity, or from which the organisms could be removed easily. But the low surface energy of fluoropolymers and the difficulty in bonding them to the substrate make it necessary to utilize special adhesives or treatments in order to obtain the required adhesion to the substrate. Several techniques have been developed for modifying polymer surfaces to improve their dispersibility in solvent of paint and adhesion properties without altering their bulk properties.<sup>1</sup> These include chemical modification<sup>2</sup> and exposure to flames, low pressure nonequilibrium plasma<sup>3,4</sup> and irradiation,<sup>5</sup> which offer an attractive way to increase the polarity of the polymer surface by creating reactive surface groups.<sup>6,7</sup> The application range of PTFE can be extended if all possibilities of increasing the concentration and varying the nature of functional groups are employed. This includes use as additives in lubricating greases, oils, and films; additives in antifriction and anticorrosion coatings; as mold-release agents in antifouling<sup>8–10</sup>; in noise reduction of low-surface-energy coatings<sup>11</sup>; in maintenance-free slide bearing ma-

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terials; and as additives in glass-fiber-reinforced thermosets. The increase in the surface free energy of the PTFE powder with the irradiation dose diminishes the oil repellency and reduces the particle size of PTFE so dramatically that homogeneous incorporation into other materials is possible. Consequently, the special properties of PTFE, such as its particular release and lubricating properties, as well as its chemical resistance, can be favorably combined with desirable properties of the other materials.

The purpose of this article is to study the incorporation of functional groups to the molecular fluoropolymers by  $\gamma$ -ray irradiation treatment at various dose. The wettability, the evaluation of  $r_s^d$  values, and the nondispersive water-solid interaction energy  $I_{sw}$  were investigated and compared by means of a one-liquid and a two-liquid method.

## EXPERIMENTAL

### Materials

PTFE powder of 5–10  $\mu\text{m}$  size and sheet in the size of  $30 \times 10 \times 1$  mm made by Chenguang Research Institute of Chemical Industry of the Ministry of Chemical Industry (China) were used in this study.

### $^{60}\text{Co}$ $\gamma$ -ray Irradiation Modification of PTFE

The irradiation of PTFE powder and sheet were performed with a  $^{60}\text{Co}$   $\gamma$ -ray source in the presence of air. The materials were put into a glass tube and irradiated at a rate of  $2.6 \times 10^3$  Gy/h from  $2 \times 10^2$  to  $3.5 \times 10^5$  Gy, and then the polymer surfaces were washed by distilled water and dried in a desiccator with silica gel at  $25^\circ\text{C}$ .

### Contact Angle Measurement

The contact angles of various liquids on the irradiated PTFE sheet (after irradiation 4 days) were measured by a goniometer–telescope system at  $25^\circ\text{C}$ . The liquid droplet of 1.28 mm diameter on the PTFE sheet was adjusted with a microscopic by holding the spring of the droplet. The contact angle was measured when the liquid droplet rested on the surface, as observable with the naked eye. For each sample, 10 measurements were averaged by changing the place of the liquid drops. Distilled water, 3.5%-salt seawater (in-

cluding 2.4% NaCl, 0.5%  $\text{MgCl}_2$ , 0.4%  $\text{Na}_2\text{SO}_4$ , 0.11%  $\text{CaCl}_2$ , 0.07% KCl, and 0.02%  $\text{NaHCO}_3$ , etc.), 1% norgine base (2.5 M NaOH) solution, 1% sodium alginate water solution, and paraffin liquid were used as liquids for the one-liquid method.<sup>12</sup> The tested plates were transferred to an optical cell and covered with hydrocarbon. The saturated hydrocarbons for the two-liquid method were *n*-hexane and cyclohexane of commercial spectroscopic-grade solvents, which were used as probe liquids by measurement of contact angles of water drops. The dispersion force component of surface tension  $r_s^d$  and the nondispersive interaction energy at the water–solid interface  $I_{sw}$  were evaluated by the analysis of the contact angles of water drops in hydrocarbon. The dispersive and polar components of the surface energy are derived from the following equations<sup>13</sup>:

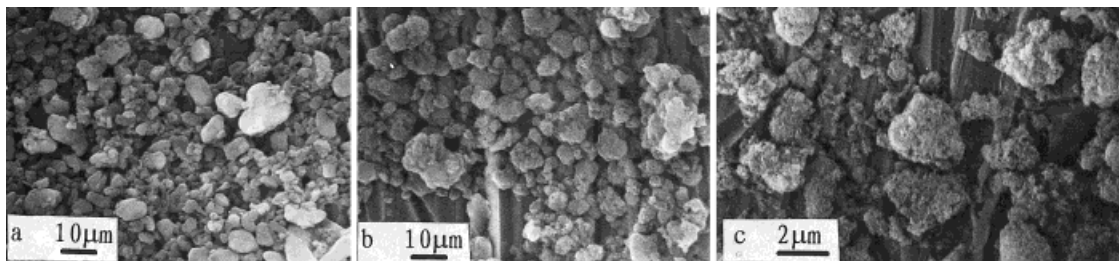
$$r_s^d = \frac{(r_{H_1} - r_{H_2}) - (r_{H_1w} \cos \theta_1 - r_{H_2w} \cos \theta_2)}{2(r_{H_1}^{1/2} - r_{H_2}^{1/2})}$$

$$I_{sw} = \frac{1}{r_{H_1}^{1/2} - r_{H_2}^{1/2}} \{ [r_{H_2}^{1/2} - (r_w^d)^{1/2}] \times (r_{H_1} - r_w - r_{H_1w} \cos \theta_1) - [r_{H_1}^{1/2} - (r_w^d)^{1/2}] \cdot (r_{H_2} - r_w - r_{H_2w} \cos \theta_2) \}$$

where  $r_{H_1}$  and  $r_{H_2}$  are the surface energy of the wetting liquid (24.9  $\text{mN m}^{-1}$  for  $\text{C}_6\text{H}_{12}$  and 18.7  $\text{mN m}^{-1}$  for  $\text{C}_6\text{H}_{14}$ ),  $r_w$  and  $r_w^d$  are the surface energy of water (72.7  $\text{mN m}^{-1}$ ) and its dispersive component (23.0  $\text{mN m}^{-1}$ ), and  $r_{H_1w}$  and  $r_{H_2w}$  are the interfacial energy for water– $\text{C}_6\text{H}_{12}$  (49.9  $\text{mN m}^{-1}$ ) and water– $\text{C}_6\text{H}_{14}$  (49.3  $\text{mN m}^{-1}$ ).  $\theta_1$  and  $\theta_2$  are the contact angles of hydrocarbons liquid on the sample in water.

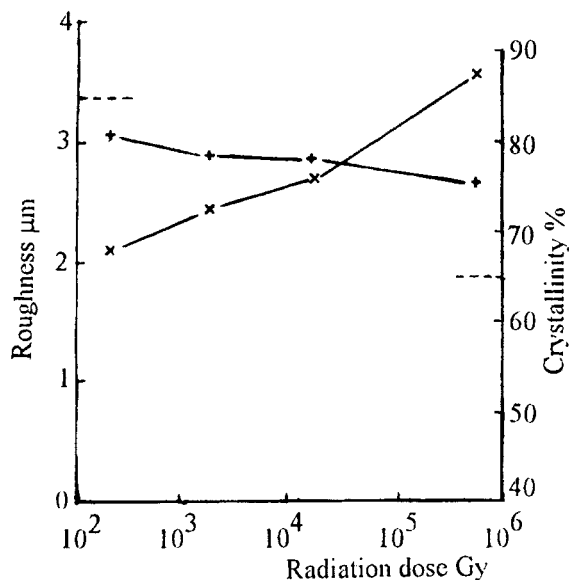
### Analytical Measurements

Reflection infrared measurements [Nicolet Co. 10DX Fourier transform infrared (FTIR) equipment] were conducted on the sheet samples of PTFE (after irradiation 4 days). To obtain more information about the surface topography, scanning electron microscopy (SEM) observation of the powder samples (after irradiation 4 days) by a TEM-1200EX at 40 kV acceleration potential and a surface profilometer BCJ-2 model (central line average on sheets) were performed. X-ray diffraction (XRD) methods have been widely used in studying the crystallinity.<sup>14</sup> A graphic multiple peak resolution method in



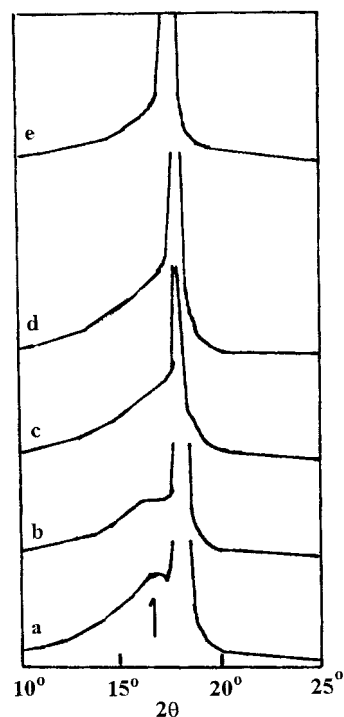
**Figure 1** Topograph of irradiated PTFE powder: (a) untreated PTFE; (b)  $2 \times 10^3$  Gy; (c)  $3.5 \times 10^5$  Gy.

estimating crystalline structures by wide angle X-ray scattering (WAXS) is introduced in this work. The degree of crystallinity determined by XRD is calculated with the correction factors of the crystallinity formula for the crystalline and amorphous peaks by a previously established method.<sup>15</sup> The XRD patterns of the sheet samples were scanned using a D/Max-RB diffractometer, the diffractometer that is equipped with a graphite monochromator gives 50 kV  $\text{CuK}\alpha$  radiation at 30 mA. The following quantitative relationship is found between number-average molecular weight of polytetrafluoroethylene and the heat of crystallization in the molecular weight  $\bar{M}_n = 2.1 \times 10^{10} \Delta H_c^{-5.16}$ , where  $\bar{M}_n$  is number-average molecular weight, and  $\Delta H_c$  is the heat of crystallization. This relationship provides a simple rapid and reliable method for

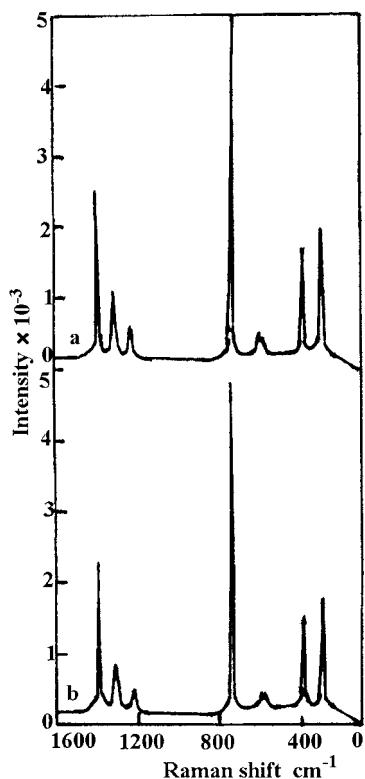


**Figure 2** The effect of the irradiation dose on the surface roughness and crystallinity of PTFE: (----) no radiation; (+) roughness; (x) crystallinity.

measuring the molecular weight of PTFE.<sup>16</sup> Heat crystallization of PTFE has been studied using a differential scanning calorimeter (DSC-2C model, P. E. Co.), and about 5 mg of polymer powder was used for this experiment. The experimental techniques used to measure the crystalline PTFE phase were FT-Raman spectroscopy (Nicolet Raman 910) and an E-115 electron spin resonance (ESR) spectrometer (measurement in the X-band region at a frequency  $\nu = 9.48$  GHz, using DPPH to calibrate the  $g$ -factor and the susceptibility). For the powder sample, the mass in the ESR cell was about 2 mg. The ESR spectra were recorded in 5 mW microwave power at 15°C.



**Figure 3** XRD pattern of irradiated PTFE: (a) 0, (b)  $2 \times 10^2$ , (c)  $2 \times 10^3$ , (d)  $2 \times 10^4$ , and (e)  $3.5 \times 10^5$  Gy.



**Figure 4** The Raman shift of PTFE: (a) untreated; (b)  $3.5 \times 10^5$  Gy.

### Frictional Coefficient Measurement

The frictional coefficient of samples (after irradiation 4 days) was determined by a Kyowa drive friction precise measuring apparatus (DFPM). The fixed PTFE sheets in air were immersed in a box of 1% sodium alginate solution or seawater, and PTFE was immersed into sodium alginate solution for about 10 min, then taken out and put into seawater test box and slid against a stationary GCr15 bearing steel ball (3 mm in diameter) at a velocity of  $0.23 \text{ mm s}^{-1}$  and a load of 0.49 N, respectively.

## RESULTS AND DISCUSSION

### Modification of PTFE and Analysis

$^{60}\text{Co}$   $\gamma$ -ray irradiation with a dose of about  $3.5 \times 10^5$  Gy caused such an embrittlement of PTFE

that it could be a medium particle size of  $2 \mu\text{m}$  of powder by mass distribution. In order to obtain some understanding of the physical nature of the surfaces, scanning electron micrographs were obtained for virgin and irradiated particles of PTFE. It was shown that untreated PTFE particle surface was smoother, but a pit on the irradiation PTFE particle appeared, and the particle size was smaller at  $2 \times 10^5$  Gy (Fig. 1). The surface roughness center line average (CLA) Ra ( $\mu\text{m}$ ) of PTFE sheet decreased from 3.3 to  $2.8 \mu\text{m}$  (Fig. 2) with an increasing irradiation dose. The XRD pattern shows that the amorphous peak width was reduced by irradiation (Fig. 3); thus, the crystallinity increased from 65.3 to 86.7% with the increasing irradiation dose (Fig. 2). The irradiation process increased the crystallinity of PTFE, and the difference in crystal structure of these polymers might affect their surface properties. The Raman activity of the spectra of these bands was the same in the phase II of PTFE after irradiation (Fig. 4), the phase II helix may be visualized most easily as a planar zigzag chain, which is twisted so that a  $180^\circ$  rotation about the chain axis occurs for every 13th  $\text{CF}_2$  group.<sup>17</sup>

The higher the irradiation dose, the smaller the average molecular weight  $\bar{M}_n$  of the PTFE; thus, a decrease of the average molecular weight of PTFE after irradiation was observed (Table I). The experimental value for the g-factor of the derivative of the ESR signal is 2.016 for irradiated PTFE ( $2 \times 10^4$  Gy dose) powders. This indicates that the number of free radicals increases in PTFE after  $\gamma$ -ray irradiation.

$^{60}\text{Co}$   $\gamma$ -ray irradiation on PTFE mainly led to degradation of the polymer because many C—C bonds of PTFE broke up to produce a great deal of free radicals, which could be proven by ESR in terms of the surface oxidation of PTFE in air. Surface groups formed by irradiation were subsequently hydrolyzed to carboxyl groups in the presence of air humidity. IR spectroscopy enables the detection of carboxyl groups. The IR spectra indicate that the characteristic C—H group was generated below 2 kGy dose (Table II). A higher irradiation dose caused other hydrophilic groups, such as —OH, —COOH, and —COH, and an

**Table I** The Average Molecular Weight of Irradiated PTFE by the Suwa Equation

| Radiation Dose/Gy | 0                  | $2 \times 10^2$    | $2 \times 10^3$    | $2 \times 10^4$    | $3.5 \times 10^5$  |
|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| $\bar{M}_n$       | $1.78 \times 10^7$ | $6.92 \times 10^6$ | $1.63 \times 10^6$ | $5.57 \times 10^4$ | $3.01 \times 10^4$ |

**Table II IR Data of Irradiated PTFE by the Reflection Method**

| Wave Number/cm <sup>-1</sup> | Radiation Dose/Gy   |                     |                     |                       |
|------------------------------|---------------------|---------------------|---------------------|-----------------------|
|                              | 2 × 10 <sup>2</sup> | 2 × 10 <sup>3</sup> | 2 × 10 <sup>4</sup> | 3.5 × 10 <sup>5</sup> |
| 1446–1451                    | C—H                 |                     |                     | C—H                   |
| 1531                         |                     |                     |                     | —CF—CF <sub>2</sub>   |
| 1550                         |                     |                     | C—H                 | C—H                   |
| 1567                         |                     | C—H                 |                     |                       |
| 1782                         |                     |                     | —COOH, —COH         | —COOH, —COH           |
| 2284                         |                     |                     | —OH, —COOH          |                       |
| 2933                         |                     |                     |                     | —OH                   |
| 3018                         |                     |                     |                     | —COOH                 |
| 3414                         |                     |                     |                     | —COOH                 |
| 3439                         |                     |                     |                     | —OH                   |

increasing concentration of carboxyl groups. At a high dose, of more than 20 kGy, hydrogen bonding groups were obtained on the PTFE surface. Furthermore, the associated behavior suggested that zones of both near-surface-associated carboxyl end groups and isolated carboxyl end groups in the bulk of the polymer exist.

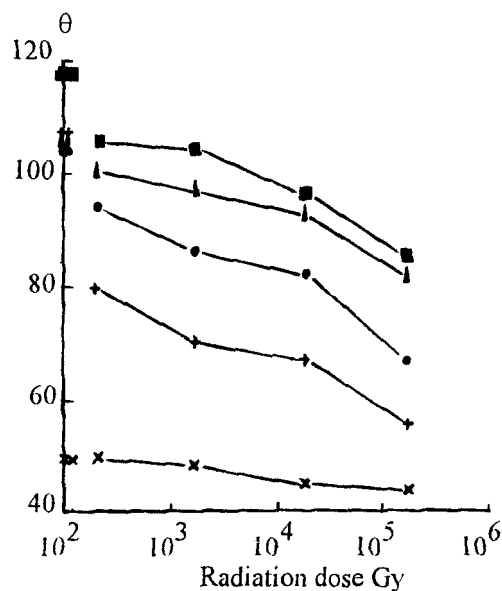
#### Wetting and Friction Coefficient of Modified PTFE

Despite incomplete theoretical background and many experimental difficulties, the contact angle measurement has been used extensively to elucidate the specific surface chemical changes imparted by surface treatments of specimens. The change in surface energy was assessed by measurement of the contact angle. Figure 5 shows the evolution of the contact angle (one-liquid method) as a function of the dose.

Untreated PTFE has a contact angle of 104–119° to some aqueous liquids of water, seawater, norgine, and sodium alginate but a contact angle of 51° to nonpolar liquid of paraffin liquid. In all cases of the increasing dose, the contact angle was reduced for any liquids. In contact angles to water, norgine are smaller than that to their salt solution containing Na<sup>+</sup>, Ca<sup>2+</sup>, or Cl<sup>-</sup>, such as seawater and sodium alginate. But the contact angle to nonpolar liquid (paraffin liquid) changed slightly with the increasing dose. This shows that hydrophobic groups of surface was less variable. The wettability of PTFE is increased by  $\gamma$ -ray irradiation. With the increasing dose, the friction coefficient increased in any systems because of action enhancement on PTFE surface (Fig. 6). Before the 2 kGy irradiation dose, the friction co-

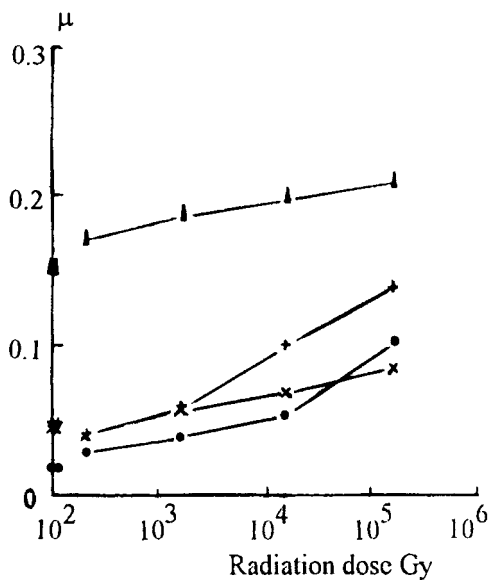
efficient and contact angles on PTFE slightly changed.

PTFE has a higher friction coefficient in the sodium alginate solution system than in the other 3 systems. This is because the high viscosity of sodium alginate solution and bond of the sodium alginate–PTFE interface cause large inner friction of liquid and interface friction despite the fact that PTFE has almost the same contact angle to sodium alginate and seawater. The high liquid



**Figure 5** Contact angles ( $\theta$ ) to some liquids versus irradiation dose of PTFE: (■) sodium alginate; (■) untreated PTFE for sodium alginate; (▲) seawater; (▲) untreated PTFE for seawater; (●) water; (●) untreated PTFE for water; (+) norgine; (++) untreated PTFE for norgine; (×) paraffin liquid; (×) untreated PTFE for paraffin liquid.

interface energy of seawater and sodium alginate therefore contributes to the lower friction on PTFE-covered sodium alginate in seawater system. Table III shows that the dispersive and polar components of surface energy did not change from 0.2 to 2 kGy, but it increased greatly after the 20 kGy dose. For a 20 kGy dose,  $I_{sw}$  increased rapidly, reaching a value of  $6.59 \text{ mN m}^{-1}$ . This confirms that the polar component of the surface free energy is increased by  $\gamma$ -ray irradiation treatment of PTFE surface.  $I_{sw}$  is considered to be mainly due to hydrogen bonding, and in some cases it is also due to dipole-dipole interaction. Moreover, the increase of  $r_s^d$  of dispersive component may be reasonable because the functional groups such as  $-\text{OH}$ ,  $-\text{COOH}$ , and  $-\text{COH}$ , have larger polarizabilities than  $\text{C}-\text{H}$  bonds, which should contribute to an increase in the dispersion force if other factors remain constant. The irradiation of PTFE induces an increase in the wettability and decrease in the particle size only at high dose. The increasing number of groups and concentration of carboxyl groups caused an increase of surface free energy on the PTFE surface. The increase in the surface free energy and wettability of PTFE with the irradiation diminishes the water, seawater, norgine solution, sodium alginate solution,



**Figure 6** Frictional coefficient ( $\mu$ ) versus irradiation dose of PTFE: (▲) in sodium alginate; (▲●) untreated PTFE in sodium alginate; (+) in seawater; (++) untreated PTFE in seawater; (●) PTFE covered sodium alginate in seawater; (●●) sodium alginate thin film of untreated PTFE in seawater; (×) in air; (××) untreated PTFE in air.

**Table III** The Dispersive and Polar Components of the Surface Energy of Irradiated PTFE by the Two-Liquid Method

| Sample             | $r_s^d/\text{mN m}^{-1}$ | $I_{sw}/\text{mN m}^{-1}$ |
|--------------------|--------------------------|---------------------------|
| Untreated PTFE     | 28.42                    | 3.93                      |
| $2 \times 10^2$ Gy | 25.72                    | 3.84                      |
| $2 \times 10^3$ Gy | 28.42                    | 3.94                      |
| $2 \times 10^4$ Gy | 36.07                    | 6.59                      |

and paraffin liquid repellency of PTFE so much that homogeneous incorporation into solvent systems or into other polymers is possible. Consequently, the special properties of PTFE, such as its particular release and lubricating properties, as well as its chemical resistance, can be favorably combined with desirable properties of other polymers.

## CONCLUSION

PTFE is degraded by  $^{60}\text{Co}$   $\gamma$ -ray irradiation in air into a finely dispersed powder modified with carboxyl groups such as  $\text{C}-\text{H}$ ,  $-\text{OH}$ ,  $-\text{COOH}$ , and  $-\text{COH}$ . A higher irradiation dose on PTFE caused an increasing concentration of carboxyl groups and frictional coefficient and a reduced contact angle to some liquid systems. The optimum irradiation dose for PTFE surface modified in air is 20 kGy when the polar component and the dispersion component of the surface free energy increased, while the particle size decreased. So the special properties of PTFE, such as its particular release and lubricating properties, as well as its chemical resistance, can be effectively retained. The  $\gamma$ -ray irradiation technique can be used to modify the inert PTFE surface to improve the dispersibility in solvent of paint, making it possible to be used as additive in antifriction, anticorrosion,<sup>18</sup> antifouling,<sup>19</sup> lubrication, drag,<sup>20</sup> and noise reduction coatings.

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