/N-27
2580
11 P

Surface Energy Changes Produced by Ultraviolet-Ozone Irradiation of Poly(methylmethacrylate), Polycarbonate and Polytetrafluoroethylene

A.B. Ponter
University of Southwestern Louisiana
Lafayette, Louisiana

W.R. Jones, Jr.
Lewis Research Center
Cleveland, Ohio

and

R.H. Jansen
Case Western Reserve University
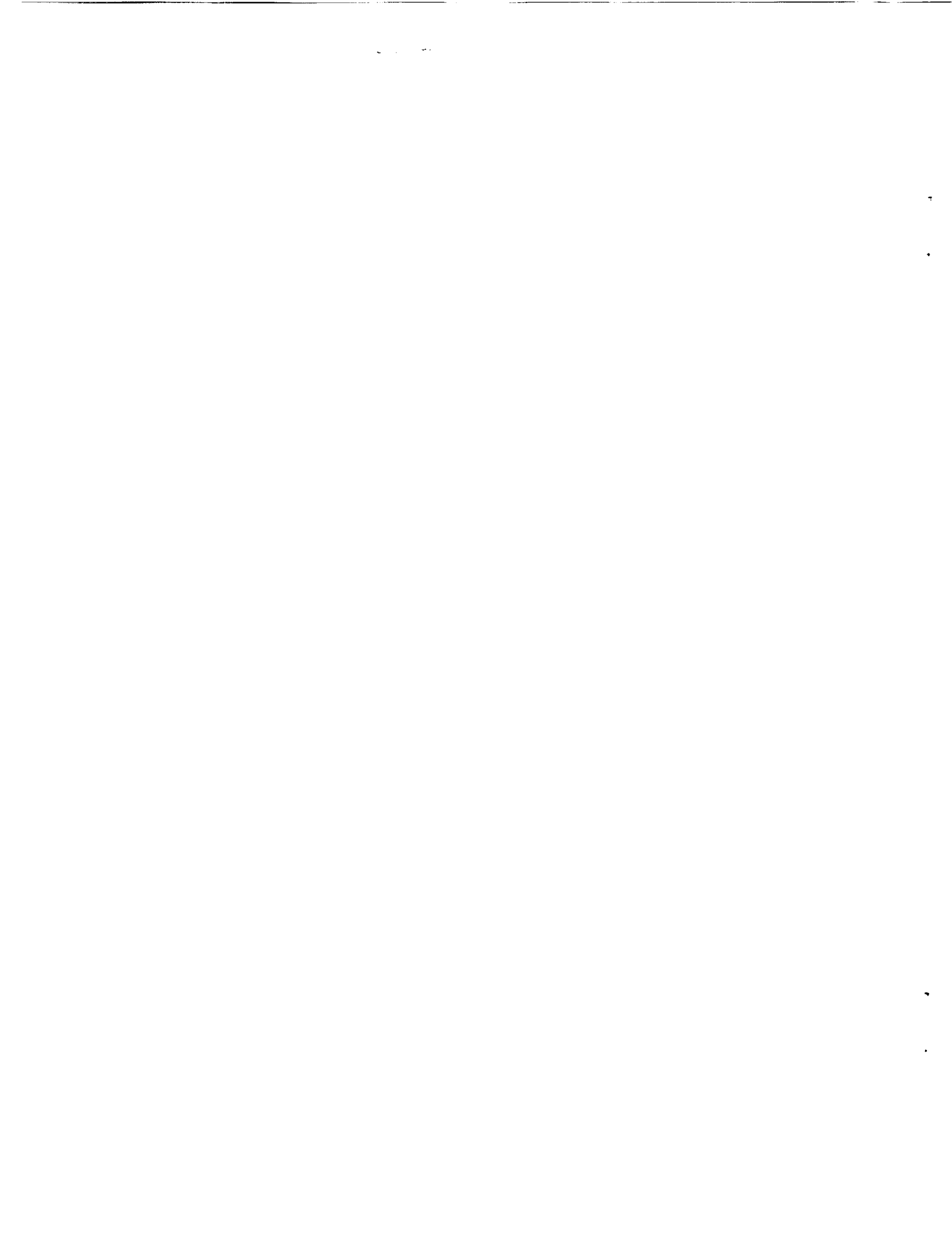*Cleveland, Ohio*

January 1994

(NASA-TM-106460)   SURFACE ENERGY
CHANGES PRODUCED BY
ULTRAVIOLET-OZONE IRRADIATION OF
POLY(METHYLMETHACRYLATE),
POLYCARBONE AND
POLYTETRAFLUOROETHYLENE   (NASA.
Lewis Research Center)   11 p

N94-28922

Unclas

G3/27   0002580

Surface Energy Changes Produced by Ultraviolet-Ozone Irradiation of Poly(methylmethacrylate), Polycarbonate and Polytetrafluoroethylene

A.B. Ponter
University of Southwestern Louisiana
Lafayette, Louisiana 70504

W.R. Jones, Jr.
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

and

R.H. Jansen
Case Western Reserve University
Cleveland, Ohio 44106

ABSTRACT

Contact angles of water and methylene iodide were measured as a function of UV/O$_3$ treatment time for three polymers: poly(methylmethacrylate) (PMMA), polycarbonate, and polytetrafluoroethylene (PTFE). Surface roughnesses were also measured. Surface free energies were then calculated using relationships developed by Kaelble and Neumann. The surface energy of polycarbonate was found to increase (~60 percent) during UV/O$_3$ treatment. However, calculations on PMMA were hampered by the formation of a water soluble surface product. On PTFE surfaces, the UV/O$_3$ treatment etched the surface causing large increases in surface roughness, rendering contact angle measurements impossible. It is concluded that care must be taken in interpreting contact angle measurements and surface energy calculations on UV/O$_3$ treated polymer surfaces.

INTRODUCTION

Ultraviolet radiation (UV) has been employed since 1960 to clean adsorbed hydrocarbons from metal and glass surfaces, but only in 1972 did Bolon and Kunz (ref. 1) recognize that enhanced cleaning occurred in the presence of ozone (O$_3$) when polymer surfaces were irradiated using wavelengths less than 300 nm. The resulting decomposition products were carbon dioxide and water. Auger electron spectroscopy revealed that no surface residues were evident except for inorganic deposits. Later Vig and Lebus (ref. 2) demonstrated that the combination of UV and O$_3$ cleaning produced carbonaceous-free surfaces in less than 1 min.

In a later study, Krusor et al. (ref. 3) when cleaning silicon surfaces with UV/O$_3$ showed the superiority of the process over the traditional wet chemistry method, giving consistently lower contamination levels. Tsuji et al. (ref. 4) developed a photoresist stripping instrument using UV/O$_3$ and showed that less damage occurred during integrated circuit processing compared with the established oxygen plasma system. They postulated that the generated ozone first reacts with the photoresist surface, which is then eliminated by the UV radiation, producing carbonyl compounds.

However, there are indications in the literature that the cleaning process may have considerable deleterious chemical and mechanical effects on polymer surfaces. Reference has been made by Lazare and Srinivasan (ref. 5) to the modification of polyethylene terephthalate (PET) films with low intensity far-UV radiation. They showed that the surface was depleted in oxygen with both a pulsed ArF laser and the low intensity UV radiation of a mercury lamp. The former process yielded a roughened surface which caused an increase in the advancing contact angle of water.

Lee and Ruckenstein (ref. 6) have investigated the surface characteristics of irradiated films of rf-sputtered poly(methylmethacrylate) (PMMA) by measuring the changes in contact angle occurring with a water drop on the surface equilibrated in an octane environment. The surface was shown to degrade and the irradiation products were found to dissolve

in the water. The extraction of these materials produced micropores in the polymer matrix which allowed water penetration into the solid. It was also noted that the water containing the soluble products caused a change in shape when added to a sessile water drop.

Most studies, however, have ignored the influence of the changing surface tension of the drop on the contact angle due to soluble decomposition products. The present investigation took this change into account when calculating the dispersion and polar components of the surface free energy from water and methylene iodide contact angles. Vig (ref. 7) has both reviewed the parameters influencing the UV/O_3 cleaning of surfaces and has described the construction and operation of a box to achieve the cleaning.

Therefore, the objective of this study was to determine the effect of UV/O_3 treatment on three polymer surfaces: poly(methylmethacrylate), polycarbonate, and polytetrafluoroethylene by measuring contact angles of water and methylene iodide as a function of irradiation time.

Experimental

Three polymers were studied, Lucite [poly(methylmethacrylate)] (PMMA), Lexan (polycarbonate), and Teflon (polytetrafluoroethylene) (PTFE). Specimens were received from the manufacturers in sheet form (6.4 mm thick) and cut into 22 mm squares. Burrs at the edges were carefully removed and the specimens were immersed in a 2 percent detergent solution (Micro, Cole Parmer Instrument Company, Chicago, Illinois) and placed in an ultrasonic bath for 2 min before being washed repeatedly with distilled water. The samples were further irrigated with methyl alcohol (liquid chromatography quality) being finally washed five times again in water and then placed in an oven at 110 °C (230 °F). The water was pre-pared by distilling deionized water in a unit which allowed the liquid surface to be continuously removed. This unit produces water with a surface tension of 72.6 to 72.8 dynes/cm at 20 °C. After residing in the oven for 24 hr, the samples were trans-ferred to a desiccator to cool to room temperature. They were then placed in an UV/O_3 generator apparatus (UVOCS, Inc., Montgomeryville, Pennsylvania) described by Vig (ref. 7), being positioned to receive identical radiation. The polymers were then irradiated separately to avoid cross contamination of any volatile product.

Pairs of samples were investigated. One of the irradiated samples was transferred from a desiccator immediately to the contact angle cell, while a second specimen was immersed in a beaker containing 50 ml of distilled water. After 24 hr, the surface tension of the solution was determined using a ring tensiometer. Then this specimen was further immersed in purified water for another 24 hr before being transferred again to the oven (110 °C) (230 °F) where it was held at temperature for at least 24 hr.

The polymer sample was then positioned in the contact angle cell (Ramé-Hart Model 100-00) through which either a dry nitrogen or a water saturated nitrogen stream continuously flowed. A microsyringe was used to place either a water drop or a methylene iodide drop on the polymer surface with sufficient volume to provide a base of more than 0.6 cm. Good and Koo (ref. 8) and Yekta-Fard and Ponter (ref. 9) have shown that below this value, the advancing contact angle is a function of drop size. Advancing contact angles were measured ensuring that the needle of the syringe remained in the drop during observa-tions as discussed by Good (ref. 8). Determinations were made under three different conditions:

1. For the dry irradiated surface in a dry nitrogen atmosphere,

2. For the irradiated surface washed free of soluble product, dried and placed in a dry nitrogen atmosphere, and

3. For the irradiated surface immersed in water for over 24 hr to ensure a saturated surface in a water-saturated nitrogen atmosphere.

All measurements reported are the average of at least four determinations which agreed within ±1°, all taken at room tem-perature (~25 °C).

The arithmetic average roughnesses of the polymer surfaces were determined using a profilometer (Dektak 3030, Veeco Instruments Inc., Santa Barbara, California). It was observed in preliminary experiments that the polycarbonate and PMMA samples were smooth (Ra <200Å) and nearly homogeneous and that the roughness increased slightly at long irradiation times. In contrast, the as received PTFE surfaces showed high (Ra >20000Å) and heterogeneous roughnesses. The water contact angles on the PTFE surfaces were 113 to 118° in contrast to the accepted value of 108° for very smooth surfaces as reported by Dann (ref. 10) and Vergara et al. (ref. 11). To reduce the roughness of the PTFE surfaces, two procedures were

adopted: (1) pressing between optical glass plates at a temperature of 204 °C (400 °F) for 24 hr, and (2) micropolishing using alumina or diamond pastes. Details have been given elsewhere (ref. 12).

Surface Free Energy Calculations

Two methods were employed to calculate the surface energies of the polymers from contact angle data. The first, described by Esumi et al. (ref. 13) uses Kaelble's (ref. 14) equation for the work of adhesion (W_a) between a liquid and a solid

$$W_a = \gamma_\ell(1 + \cos\theta) = 2\left[(\gamma_s^d \gamma_\ell^d)^{1/2} + (\gamma_s^p \gamma_s^p)^{1/2}\right] \tag{1}$$

where γ_ℓ is the surface tension of the liquid; θ is the liquid-solid-air contact angle; γ_ℓ^d is the dispersion component of γ_ℓ; and γ_ℓ^p is the polar component of γ_ℓ; γ_s is the total surface free energy of the solid; and γ_s^d and γ_s^p are the dispersion and polar components of the solids, respectively. The contact angles for two liquids for which the dispersion and polar components of the surface tension are known, allow from the resulting simultaneous equations, the determination of the dispersion and polar components of the solid.

The second method used was based on Neumann's (ref. 15) equation of state:

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_s}{\gamma_\ell}}e^{-\beta(\gamma_\ell - \gamma_s)^2} \tag{2}$$

where $\beta = 0.0001247$.

The two liquids selected were water and methylene iodide (CH_2I_2).

RESULTS AND DISCUSSION

Preliminary experiments were carried out to determine if soluble irradiation products would be formed which would change the surface tension of the liquid drop (γ_ℓ) residing on the surface. Samples were irradiated for varying times up to one hour to determine if new chemical products were being formed at the surface. Irradiated polymer samples were then placed in 50 ml of distilled water for 24 hr. of the solution was then measured using a ring tensiometer. No changes in γ_ℓ were observed with polycarbonate and PTFE, but for the PMMA samples, reductions of up to 10 dynes/cm resulted, as shown in figure 1.

Poly(methylmethacrylate)

As stated, contact angles of water on PMMA surfaces were measured under three well-defined conditions and are illustrated in figure 2. Similarly, the contact angles in figure 3 and table I were measured using methylene iodide. From these data the solid surface energy of PMMA was determined using Kaelble's equation (1) as shown in table III and figure 4. It is important to note that the surface tension of the aqueous drop was substituted for that of pure water in the calculation. However, Byrne et al. (ref. 16) has shown that the use of solutions in contact angle measurements for determining solid surface energies is unreliable. Although contact angles were predicted using Neumann's equation of state (eq. 2), shown in figure 5, this equation can not be reliably used to determine solid surface energies from contact angles of binary systems. Therefore, the calculated surface energy values are still not valid although the influence of surface tension change caused by the irradiation products has been taken into account. By the same reasoning, it can be seen that the results of Esumi et al. (ref. 13) and other workers are equally faulted.

Polycarbonate

For the polycarbonate surface, no change in surface tension of water (in which the polycarbonate was immersed) was observed and the contact angle and surface energy data are presented in figs. 6 and 7 as well as table II and IV. These data indicate that the UV/O_3 treatment causes an increase in polycarbonate surface energy to ~60 to 61 ergs/cm^2 (approximately a 60 percent increase) after 2 min of irradiation. Longer irradiation times (to 120 min) resulted in further increases to ~66 to 68 ergs/cm^2.

Polytetrafluoroethylene

For PTFE, a significant increase in surface roughness was observed with increasing irradiation time, and the measured contact angles could not be used in calculations since Morra et al. (ref. 17) have reported that the increased roughness causes air entrapment. PTFE samples, as received, had an R_a surface roughness of 21000 Å and a contact angle of 114°, whereas a PTFE sample that had been irradiated for one hour had corresponding values of 40800 Å and 133°.

SUMMARY

Contact angles of water and methylene iodide were measured as a function of UV/O_3 treatment time for three polymers: poly(methylmethacrylate) (PMMA), polycarbonate, and polytetrafluoroethylene (PTFE)). In addition, surface roughnesses were also measured. Surface free energies of the polymers were then calculated using empirical relationships developed by Kaelble and Neumann. Results can be summarized as follows.

1. UV/O_3 treatment of PMMA generates a water soluble surface product that affects contact angle measurements.

2. UV/O_3 treatment of polycarbonate does not produce a water soluble product but does cause an increase (~60 percent) in surface energy.

3. UV/O_3 treatment of PTFE etches the surface and causes an increase in surface roughness which prevents reliable contact angle measurements.

CONCLUSIONS

The following conclusions can be drawn from this study:

1. Caution must be observed when using UV/O_3 cleaning of polymer surfaces because of possible surface chemical reactions and/or etching producing roughness changes.

2. Care must be taken when applying Kaelble's or Neumann's equations for surface energy calculations when polymer surfaces have been UV/O_3 treated.

REFERENCES

1. Bolon, D.A. and Kunz, C.O.: Polym. Eng. Sci., Vol. 12, 109 (1972).

2. Vig, J.R. and Lebus, J.W.: IEEE Trans. Parts, Hybrids and Packag., Vol. PHP-12, pp. 365-370, 1976.

3. Krusor, B.S., Biegelsen, D.K., Yingling, R.D., and Abelson, J.R.: J. Vac. Sci. Technol., Vol. B7, p. 129, 1989.

4. Tsuji, O., Tatsuta, T., and Deguchi, K.: Proceedings of the 7th International Symposium on Plasma Chemistry, edited by C.J. Timmermans (Eindhoven University of Technology, Eindhoven, Netherlands, 1985) Vol. 3, pp. 1055-1060.

5. Lazare, S. and Srinivasan, R.: J. Phys. Chem., Vol. 90, p. 2124, 1986.

6. Lee, S.H. and Ruckenstein, E.: J. Colloid Interface Sci., Vol. 117, p. 172, 1987.

7. Vig, J.R.: J. Vac. Sci. Technol., Vol. A 3, p. 1027, 1985.

8. Good, R.J. and Koo, M.N.: J. Colloid Interface Sci., Vol. 71, p. 283, 1979.

9. Yekta-Fard, M. and Ponter, A.B.: J. Adhesion, Vol. 18, p. 197, 1985.

10. Dann, J.R.: J. Colloid Interface Sci., Vol. 32, p. 302, 1970.

11. Vergara, F., Rose, M., and Lespinasse, R.: C. R. Acad. Sci. Ser. Vol. C269, p. 441, 1969.

12. Ponter, A.B. and Yekta-Fard, M.: J. Colloid Polym. Sci., Vol. 263, p. 673, 1985.

13. Esumi, K., Schwarz, A.M., and Zettlemoyer, A.C.: J. Colloid Interface Sci., Vol. 95, p. 102, 1983.

14. Kaelble, D.H.: J. Adhesion, Vol. 2, p. 66, 1970.

15. Li, D., Cheng, P., and Neumann, A.W.: International Symposium on Contact Angles and Wetting Phenomena, (University of Toronot, Toronto, Canada, 1990), p. 20.

16. Byrne, K.M., Ross, J.R.H., and Roberts, M.W.: Adhesion, Vol. 1, p. 19, 1977.

17. Morra, M., Occhiello, E., and Garbassi, F.: Langmuir, Vol. 5, p. 872, 1989.

TABLE I.—CONTACT ANGLES OF WATER AND METHYLENE IODIDE ON [POLY(METHYLMETHACRYLATE)] (PMMA) AS A FUNCTION OF UV IRRADIATION TIME FOR THREE CONDITIONS

UV irradiation min	Contact angle, θ, degrees				
	Water			Methylene iodide	
	Dry sample dry N_2 atmos	Soluble product removed by H_2O washing, then dried	Equilibrated with H_2O, H_2O saturated N_2 atmos	Dry sample dry N_2 atmos	Soluble product removed by H_2O washing, then dried
0	73		72	49.5	
1	69	77	79.5	46	42.5
2	70.7	76	76	48.5	44
3	73	74	71	46.5	42
4	63	77		45	41
7	56	75	70	44.5	42
10	45.3	74		49.3	38.5
12	42	75		48.5	42
15	41	72	66	48.5	47.5
20	42.3	77		57	44.5
30	48.3	77		65.5	44
40	52	88		50	42
50	58	85	67	46	47
60	61.5	91		52	44
80	66	92	71	52.5	45
100	67.5	92		51.5	45
120	68	-		48	-

TABLE II.—CONTACT ANGLES OF WATER AND METHYLENE IODIDE ON LEXAN (POLYCARBONATE) AND AS A FUNCTION OF UV IRRADIATION TIME

UV irradiation time, min	Contact angle, degrees	
	Lexan	
	Water	Methylene iodide
0	89.5	42
1	69	42
2	48	41
4	34	46
7	35	45
10	33.7	46
12	29	44
15	24.7	41
20	26	46
30	19.3	49
40	19.7	51
50	16	64
60	19	49.5
80	21	59.5
100	20.8	56.5
120	22.3	58

TABLE III.—CALCULATED SURFACE ENERGIES OF [POLY(METHYLMETHACRYLATE)] (PMMA) FOR THREE CONDITIONS USING KAELBLE'S EQUATION

UV irradiation time, min	Assuming constant $\gamma_{H2O} = 72.6$			Variable γ_{H2O}			Soluble product removed by H_2O washing, then dried		
	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s
0	28.5	9.5	38	28.5	9.5	38	28.5	9.5	38
1	30	11	41	30.5	9.5	40	33.5	6	39.5
2	30.5	10	40.5	31	8.5	39.5	33	6.5	39.5
3	30	9	39	31	7.5	38.5	33	7.5	40.5
4	29	15	44	30	12.5	42.5	35	5.5	40.5
7	28	20	48	29	16.5	45.5	33.5	7	40.5
10	23.5	30	53.5	24	25.5	49.5	35	7	42
12	22.5	33.5	56	24	27.5	51.5	33.5	7	40.5
15	23	33.5	56.5	24	28	52	29.5	9.5	39
20	18.5	36.5	55	20	29.5	49.5	32	6.5	38.5
30	15	35	50	16	28.5	44.5	33	6	39
40	24	25	49	25.5	18	43.5	37.5	1.5	39
50	27.5	19	46.5	29.5	12.5	42	33.5	3	36.5
60	24.5	18.5	43	26.5	12	38.5	37	1	38
80	25	15	40	27	9.5	36.5	36	1	37
100	26.5	13.5	40	28.5	8	36.5	36	1	37
120	28	12.5	40.5	30.5	7	37.5	-	-	-

TABLE IV.—CALCULATED SURFACE ENERGIES OF LEXAN (POLYCARBONATE) USING KAELBLE'S EQUATION

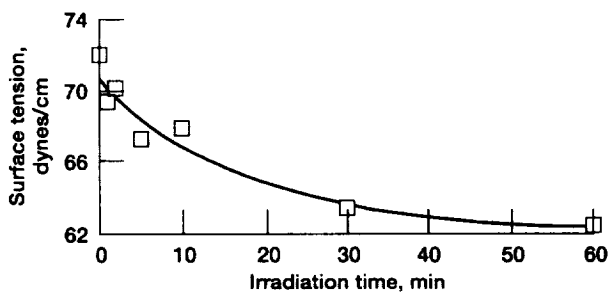| UV irradiation time, min	Surface energy, (ERGS/CM^2) Polycarbonate		
	γ_s^d	γ_s^p	γ_s
0			
1	32	10.5	42.5
2	28	25.5	53.5
4	23.5	37.5	61
7	24	36.5	60.5
10	23.5	38	61.5
12	24	40	64
15	25	41.5	66.5
20	22.5	43	65.5
30	20.5	48	68.5
40	19.5	49	68.5
50	14	49.5	63.5
60	20.5	48	68.5
80	16	49.5	65.5
100	17	49.5	66.5
120	16.5	49.5	66

Figure 1.—Change in the surface tension of water after exposure to irradiated PMMA.
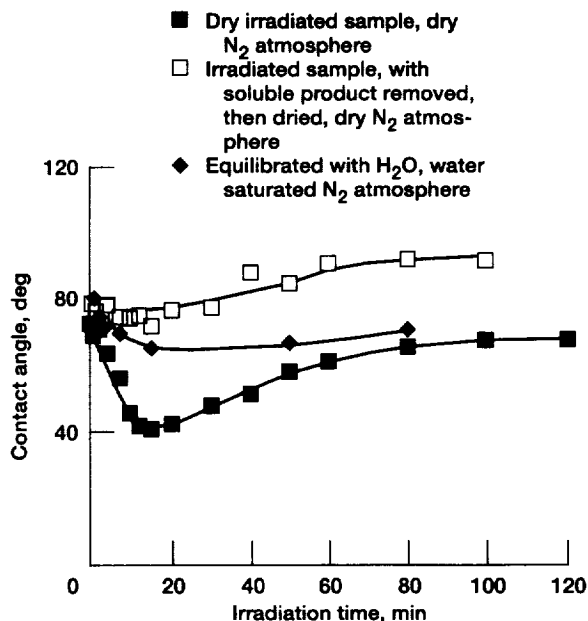

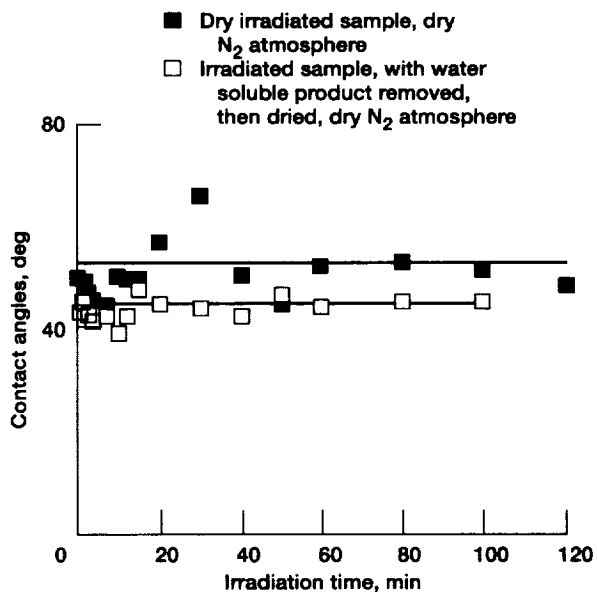Figure 2.—Contact angles of H_2O on PMMA for three different conditions.

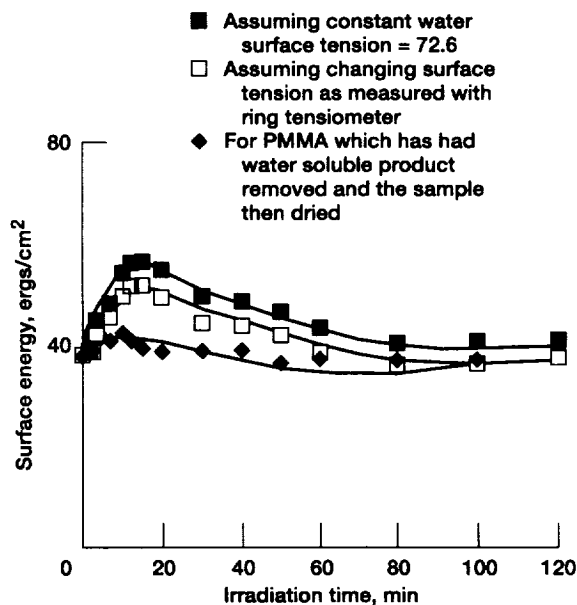Figure 3.—Contact angles of methylene iodide on PMMA for two different conditions.

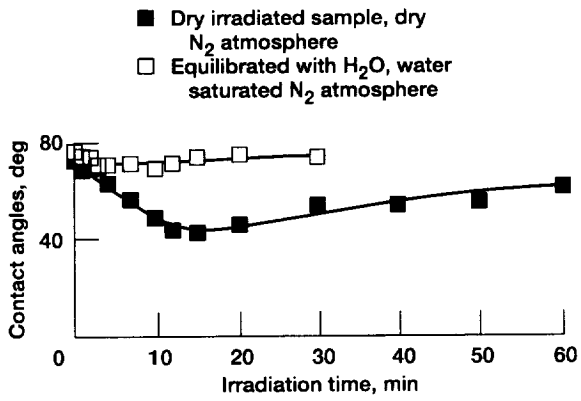Figure 4.—Surface energy of PMMA calculated by Kaelble's equation for three different conditions.

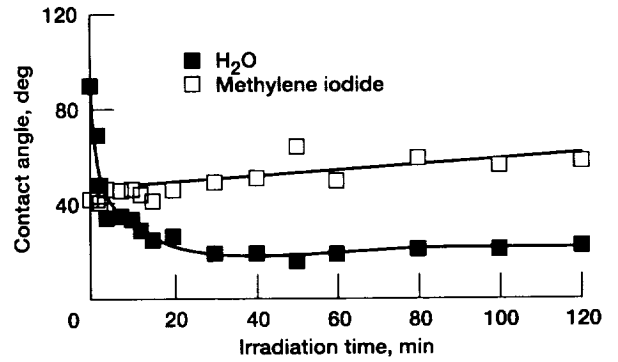Figure 5.—Contact angles of H_2O on PMMA predicted by Neumann's equation.

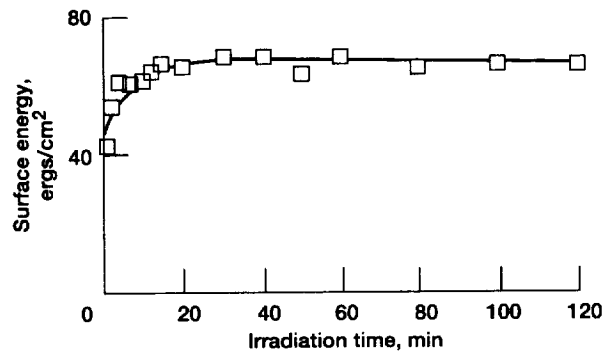Figure 6.—Contact angles of H_2O and methylene iodide on polycarbonate.

Figure 7.—Surface energy of polycarbonate calculated by Kaelble's equation.

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	January 1994	Technical Memorandum

4. TITLE AND SUBTITLE

Surface Energy Changes Produced by Ultraviolet-Ozone Irradiation of Poly(methylmethacrylate), Polycarbonate and Polytetrafluoroethylene

5. FUNDING NUMBERS

WU–505–63–5A

6. AUTHOR(S)

A.B. Ponter, W.R. Jones, Jr., and R.H. Jansen

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135–3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E–7806–1

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, D.C. 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM–106460

11. SUPPLEMENTARY NOTES

A.B. Ponter, University of Southwestern Louisiana, Lafayete, Louisiana 70504; W.R. Jones, Jr., NASA Lewis Research Center; and R.H. Jansen, Case Western Reserve University, Cleveland, Ohio 44106. Responsible person, W.R. Jones, Jr., (216) 433–6051.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category 27

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Contact angles of water and methylene iodide were measured as a function of UV/O_3 treatment time for three polymers: poly(methylmethacrylate) (PMMA), polycarbonate, and polytetrafluoroethylene (PTFE). Surface roughnesses were also measured. Surface free energies were then calculated using relationships developed by Kaelble and Neumann. The surface energy of polycarbonate was found to increase (~60 percent) during UV/O_3 treatment. However, calculations on PMMA were hampered by the formation of a water soluble surface product. On PTFE surfaces, the UV/O_3 treatment etched the surface causing large increases in surface roughness, rendering contact angle measurements impossible. It is concluded that care must be taken in interpreting contact angle measurements and surface energy calculations on UV/O_3 treated polymer surfaces.

14. SUBJECT TERMS

Polymers; Surface energy; Ozone; Ultraviolet

15. NUMBER OF PAGES

12

16. PRICE CODE

A03

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	