NRL Report 6563

Surface Effects in the Photodegradation of Polymer Films

July 5, 1967

NAVAL RESEARCH LABORATORY
Washington, D.C.

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ABSTRACT

The effect of ultraviolet irradiation in air on the wettability of polymer surfaces by liquids of known surface tensions has been studied. The polymers studied were polystyrene, poly(vinyl chloride), poly(ethylene terephthalate), poly(methyl methacrylate), and poly(butyl methacrylate). Changes in contact angles of the contact liquids used were plotted versus the time of irradiation of the polymer surface. Spectral evidence is presented to show that photodegradation products include oxygenated moieties capable of interaction with polar liquids. Polymer fragments resulting from chain scission also play an important role in wettability changes for some polymers. Extraction and spectral studies of irradiated polystyrene surfaces showed that photodegradation products include small molecules, readily removed by extraction, and oxidized (as carbonyl) polymer chains which are not readily removed from the surface.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

NRL Problem C04-04
Projects RR 001-02-43-4801 and SF 020-04-06-1201

Manuscript submitted March 7, 1967.

SURFACE EFFECTS IN THE PHOTODEGRADATION OF POLYMER FILMS

INTRODUCTION

The degradation of organic coatings exposed to natural weathering is in large measure the result of the combined action of ultraviolet light and oxygen. Photooxidation occurs in a coating to a depth dependent on the availability of oxygen and the absorbance of the coating for the incident radiation. Thus, in a coating which strongly absorbs energy incident upon it, photooxidation reactions will occur in a narrow zone at or near the exposed surface. Even in a relatively transparent coating the accessibility of the irradiated surface layers to air should result in an accumulation of degradation products in those layers. A study of these products or the effects generated by these products not only would be expected to provide information on the course of the photooxidation process but may also lead to an early indication of future photooxidative degradation within the bulk of the coating itself. Such indicators may be of prime importance in the prediction of long-term coating behavior on the basis of short-term evaluation.

Wettability of polymer surfaces by liquids of known surface tension has been shown by Zisman and coworkers (1-3) to be a convenient and useful determinant of the constitution of those surfaces. From Table 1 it can be seen that the wettability of surfaces, as indicated by contact angle measurements, varies widely depending on the nature of the surface. For example, the contact angle of water on paraffin is 108° but on polyethylene is only 94° (2). Although both materials consist of hydrocarbon chains, the lower molecular weight paraffin has more methyl terminal groups in the surface than does polyethylene. A higher concentration of the more hydrophobic methyl groups naturally leads to increased hydrophobicity (2).

The wettability of polymer surfaces is characteristic of those surfaces (1), so any chemical changes in the surface constitution will lead to changes in wettability. It has been shown by Jarvis and coworkers (4) that addition of small amounts of surface-active materials also changes the wettability of polymer surfaces. Jech (5) reported that alpha radiation changes the wettability of polystyrene by water. Ehrenberg and Zimmer (6) investigated the effect of gamma radiation in air on the wettability of a number of polymers by aqueous sodium hydroxide and found that the changes in the contact angles with irradiation depended on the nature of the polymer. Similar observations with gamma radiation were reported by Jedlinski and coworkers (7).

From a practical standpoint the importance of ultraviolet radiation in the organic coating field transcends that of the shorter wavelength radiations. The work reported here has been confined to pure polymer films which have been subjected to ultraviolet irradiation in air. Constitutive changes which have taken place as a result of irradiation have been assessed on an empirical basis by means of contact angle measurements with a variety of liquids. A rough indication of the chemical nature of the changes taking place is provided by spectroscopic and other means.

EXPERIMENTAL METHOD

Materials

The liquids used in the contact angle determinations are listed in Table 2 together with their surface tensions. These liquids were purified by distillation and percolation.

Table 1
Contact Angles on Polymer Surfaces

Liquid	Surface Tension at 20°C (dyne/cm)	Contact Angle				
		Paraffin (Ref. 2)	Polyethylene (Ref. 2)	Poly(vinyl chloride) (Ref. 3)	Polystyrene (Ref. 4)	Poly(methyl methacrylate) (Ref. 4)
Water	72.8	108	94	87	96	76
Glycerol	63.4	96	79	67	84	69
Formamide	58.2	91	77	66	80	63
Methylene iodide	50.8	66	52	36	—	42
1-Bromonaphthalene	44.6	47	35	11	15	18
Tricresylphosphate	40.9	62	44	14	18	24

Table 2
Liquids Used in Wettability Studies

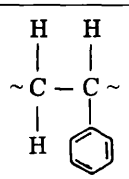
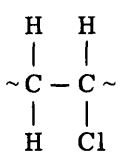
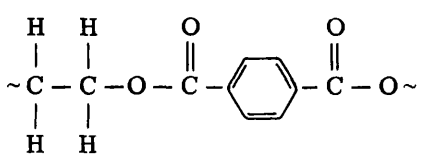
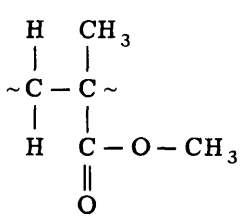
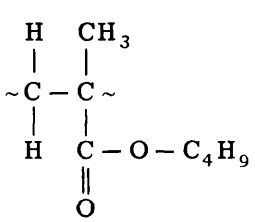
Liquid	Surface Tension at 20°C (dynes/cm)
Water	72.6
Formamide	58.2
Methylene iodide	50.8
Ethylene glycol	47.7
1-Bromonaphthalene	44.6
n-Hexadecane	27.6

The polymers studied are listed in Table 3. All were from commercial sources except poly(methyl methacrylate), which was a bulk AIBN-initiated sample prepared in this laboratory. All the polymers except poly(ethylene terephthalate) were purified by precipitation from tetrahydrofuran solutions with methanol. The poly(ethylene terephthalate) was a sample of Mylar Type A 5-mil sheet.

Apparatus

Contact angle measurements were made using a Rame-Hart NRL Model contact angle

Table 3
Polymers Studied

Polymer	Structure
Polystyrene	
Poly(vinyl chloride)	
Poly(ethylene terephthalate)	
Poly(methyl methacrylate)	
Poly(n-butyl methacrylate)	

goniometer. Ultraviolet spectra were obtained with a Perkin-Elmer Model 4000 spectrophotometer. Beckman IR-12 and Perkin-Elmer Model 21 infrared spectrometers were used to obtain infrared spectra. Where appropriate, a Wilks Scientific Corp. single beam internal reflectance attachment (Model 9000) fitted with a 45° KRS-5 reflector plate was used in conjunction with both infrared instruments. The apparatus used for vacuum irradiation experiments has been described previously (8); a General Electric Co. UA-3 350-watt medium-pressure mercury lamp was used as the radiation source.

Procedure

For wettability studies, films of all polymers except poly(ethylene terephthalate) were prepared by casting on 1 x 3 in. acid-cleaned glass slides from 4% (w/v) solutions. Tetrahydrofuran was used as the solvent for poly(vinyl chloride), and methylene chloride was the solvent for the other polymers. Poly(ethylene terephthalate) was cut into 1 x 3 in. pieces from 5-mil sheets; the surface was cleaned by detergent washing, water rinsing, and vacuum drying at room temperature. Other films were vacuum dried at room temperature for 16 hr prior to use.

Samples were irradiated for the desired time at 20 cm from the unfiltered ultraviolet source; the temperature at the sample was 30 ± 2°C. Separate samples were used for each exposure. For measuring contact angles the advancing contact angle method described by Fox and Zisman (9) was used. All contact angles reported are the average of at least 4 drops on 2 separate films, except for poly(methyl methacrylate) where for several points only 1 sample was available. Reproducibility of contact angle measurements was generally within ±2° although occasional erratic samples were encountered after 120 min irradiation, and equilibrium contact angles could not always be obtained for polar liquids on irradiated methacrylate surfaces. Equilibrium contact angles could not be obtained for formamide and ethylene glycol on poly(butyl methacrylate) after 60 min irradiation nor for water after 120 min. Similarly, equilibrium contact angles were not found for water and formamide on poly(methyl methacrylate) after 120 min irradiation. In these cases the initial values of the contact angles were reported.

In experiments in which degradation products were removed by extraction, 100-mg polymer films were cast in 45 cm^2-quartz dishes and vacuum-dried at 65°C for 24 hr. Prior to irradiation the films were covered with 5 ml of extractant for 16 hr, the extractant removed, and the film dried. After irradiation the film was extracted with a fresh 5-ml sample of liquid for 16 hr, again dried, and the cycle repeated to increase the concentration of the products in the extracts. With the polystyrene samples on which contact angles were measured between irradiations and extractions with methanol, extraction times were 30 min and drying times were 60 min in vacuum at 65°C.

The extracts were examined by ultraviolet spectroscopy. Evaporation of the extracts directly on a KRS-5 prism or aluminum foil which could be placed in contact with a KRS-5 prism allowed a determination of the spectra of the nonvolatile extractable degradation products by frustrated multiple internal reflectance (FMIR) techniques (10). Both irradiated and unirradiated films, freed from thin supports, were examined by both infrared transmission and FMIR methods. For FMIR measurements, KRS-5 prisms were used, and spectra of the surface layers of the films were obtained to a depth approximately equal to the wavelength of the incident energy.

RESULTS AND DISCUSSION

In considering the changes in wettability of polymer surfaces resulting from irradiation in air, several factors other than the nature of the products must be kept in mind:

1. Absorption coefficients of the polymer. Comparisons among polymers should be based not only on the time of irradiation but also on the energy absorbed. At a given wavelength the absorption coefficients of the different polymers studied varied considerably. Thus, if the same thickness of film of each polymer was exposed for the same period of time to 260 nm radiation, the actual amounts of energy absorbed by the surface layers would be in the order: polystyrene ≈ poly(ethylene terephthalate > poly(vinyl chloride) > poly(butyl methacrylate) ≈ poly(methyl methacrylate), as shown in Fig. 1.

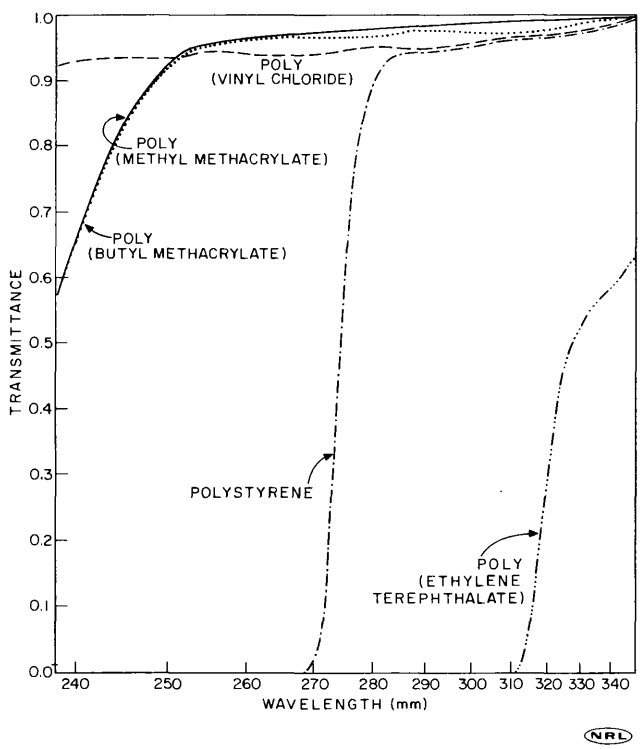


Fig. 1 - Ultraviolet spectra of polymers. Film thickness ~20μ; poly(ethylene terephthalate) 5 mil.

2. Surface roughness. The physical condition of the surface is a factor of great importance in wettability studies (1). It is possible that the somewhat erratic results found with films receiving long exposures might be due to roughening resulting from volatilization of material or from crosslinking which could produce areas of surface roughness through microscopic shrinking.

3. Dissolution of products in the wetting liquid. The effect of solubilization of degradation products by the contact liquids might also be of some concern. However, it was found that when water was placed in contact with an irradiated polystyrene surface for 30 min and then placed on an unirradiated polystyrene surface, the contact angle was found to be the same as for pure water. Similar results were obtained for formamide and ethylene glycol on irradiated and unirradiated poly(butyl methacrylate) surfaces. It would appear that either the degradation products are not surface active or insufficient quantities were dissolved by the contact liquids to affect their surface tensions. Since in measurements of contact angles the liquid is in contact with the surface for only a minute or two, it seemed unlikely that solubilization of degradation products was a serious problem in this work.

4. Miscibility of the polymer and contacting liquid. If a wetting liquid is capable of dissolving the material it wets, the solid-liquid interfacial surface tension will have a low value (2). The contact angle, then, will be lower than would be expected from the surface tension of the wetting liquid. If the wetting liquid attacks the surface rapidly, it is difficult, if not impossible, to determine an equilibrium value of the contact angle. Polymer chains altered by photodegradation may contain solubilizing groups for certain liquids; as these groups build up in the surface layers, contact angles with specific liquids may correspondingly decrease, and eventually complete wetting may occur.

5. Surface orientations. Schonhorn and Ryan (11) have shown that the wettability of polymer surfaces can be markedly different depending on the degree of crystallinity of the surface. For the polymer films used in the present work which were prepared by casting and solvent evaporation, it seems reasonable to assume an amorphous surface. Poly(ethylene terephthalate), the only polymer used in this work which was not prepared by casting, probably has some degree of surface orientation (12). In any case, changes in surface orientation occurring as a result of irradiation might well bring about changes in wettability.

Changes in the wettability of all the polymers were found to occur after ultraviolet irradiation in air; the results are discussed separately for each polymer.

Polystyrene

Irradiation of polystyrene films in air resulted in alterations in surface wettability reflected by the contact angle changes shown in Fig. 2. That the indicated variations in wettability are due to photooxidation is seen in the complete lack of change in contact angles for any of the liquids on a polystyrene film which had been irradiated 120 min in vacuum. Further support for the presence of oxygenated structures in the air-irradiated surfaces is given by the marked decrease in contact angles for the hydrogen-bonding liquids, water, formamide, and ethylene glycol, as opposed to the minor changes for 1-bromonaphthalene. Detailed identification of the products of the photooxidation of polystyrene will be the subject of another report (13).

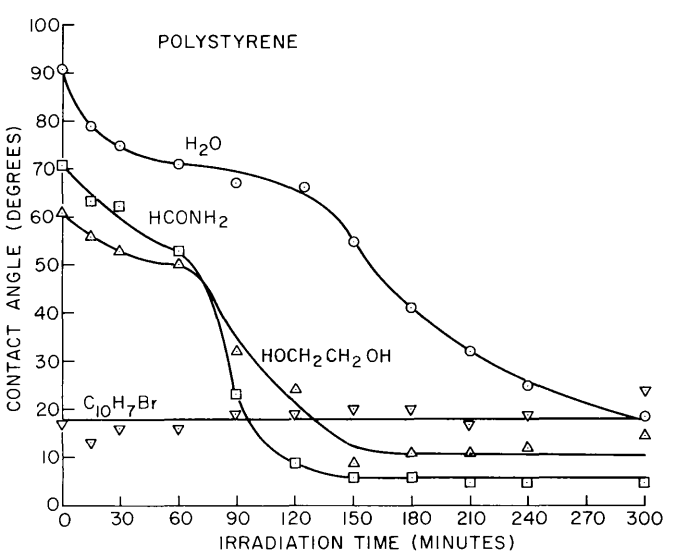


Fig. 2 - Changes in contact angles of various liquids on irradiated polystyrene

As was expected the attenuation of the incident radiation by the film resulted in photooxidation only on the exposed side of the film. This is borne out by a comparison of the frustrated multiple internal reflectance spectra obtained from either side of the exposed film. Although the exposed side of the film showed strong absorption bands in the carbonyl region at about 1725 cm^{-1}, no change was observed in the side of the film opposite the radiation source. The products of photooxidation could not have been formed at distances greater than about 6μ into the film, since the depth of penetration of infrared radiation producing these spectra roughly corresponds to the wavelength of the radiation, about 6μ. The buildup in intensity of the carbonyl band during irradiation was readily observed.

More than one product is present in the surface of the irradiated film. It was found that washing the exposed film with aqueous detergent solution, followed by rinsing with water and vacuum drying, resulted in an increase, relative to the unwashed film, in the contact angles with polar liquids. Thus some of the material capable of affecting the contact angles could be removed from the surface. This ready removal could also be accomplished by extraction of the exposed surface with methanol or other polar solvents in which polystyrene itself is insoluble. The effect of methanol extraction on the contact angles of water on irradiated polystyrene can be seen in Fig. 3. During the first 90 min of irradiation methanol extraction of the film produced no significant change in the water contact angle. In longer exposures methanol extraction gave films having the same water contact angle, irrespective of irradiation time, but the unextracted films gave steadily decreasing water contact angles as the time of irradiation increased. Clearly, the irradiated surface contains at least two kinds of material capable of interaction with water. It is probable that the methanol-insoluble material consists, at least in part, of polymer chains containing carbonyl groups at various points or in the end groups (13).

From the shape of the curves in Fig. 3 it would appear that the formation of methanol-soluble material is dependent on the prior formation of nonextractable products. Beyond about 90 min irradiation the surface must become saturated with the nonextractable materials, at least in reference to their interaction with water. To the extent that the contact angle reflects a constitution change in the surface, it is evident that

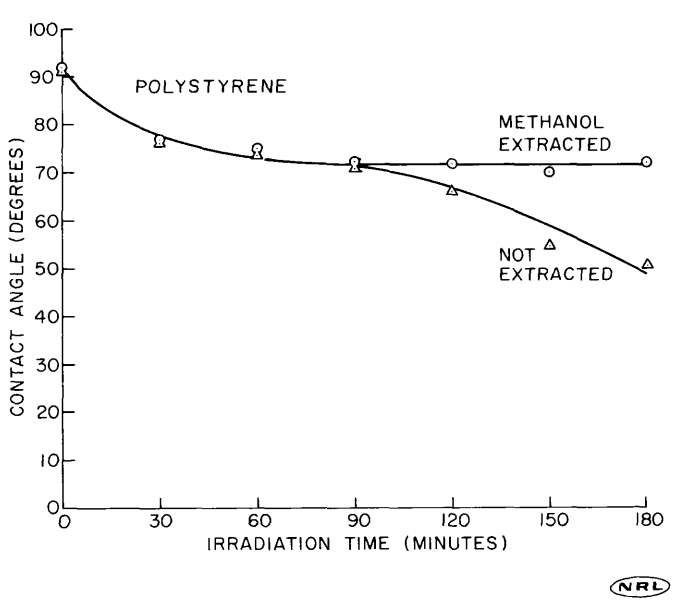


Fig. 3 - Effect of photooxidation product on contact angle of water on irradiated polystyrene

not only are measurements such as those shown in Fig. 3 related to the overall products of photooxidation but, where these products can be separated, specific effects can also be demonstrated. Thus changes in surface wettability can be a useful index of both rate and kind of weathering reactions, at least where ultraviolet light and air are the major factors. If the products formed initially are those which would continue to form during long-term exposures, then contact angle changes may be an indication of much later changes in bulk properties of the film.

Poly(vinyl Chloride)

Poly(vinyl chloride) is not a strong absorber of the ultraviolet radiation used in this work (see Fig. 1), so photodegradation should occur throughout the film. It has been reported by Kenyon (14) that ultraviolet irradiation of poly(vinyl chloride) in air results in dehydrochlorination and the appearance of carbonyl groups in the film. Chain scission has been reported to occur when photolysis is carried out in air, and crosslinking has been observed in the absence of air (15). Contact angles for a variety of liquids on poly(vinyl chloride) as a function of time of irradiation of the polymer in air are shown in Fig. 4.

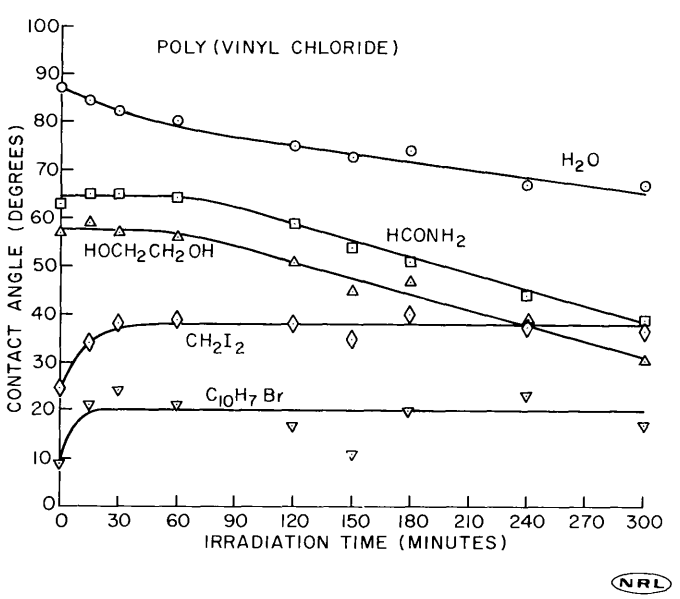


Fig. 4 - Changes in contact angles of various liquids on irradiated poly(vinyl chloride)

The contact angles of formamide and ethylene glycol changed very little during the first 60 min of irradiation, but after this time they decreased at an appreciable rate. The contact angle of water decreased from the beginning of irradiation. While all three liquids are sensitive to the presence of polar groups, it is apparent that the responses are not identical but probably depend on the nature and concentration of any polar degradation products formed. After 30 min irradiation of poly(vinyl chloride) the contact angles of methylene iodide and 1-bromonaphthalene increased to the values reported by Ellison and Zisman (3) for a pure poly(vinyl chloride) surface. The cause of this behavior is uncertain; it is possible that some impurity, present initially on the surface, is removed by irradiation. Irradiation of poly(vinyl chloride) in vacuum for 120 min also resulted in an increase in the contact angles of 1-bromonaphthalene and methylene iodide

to the values of Ellison and Zisman (3). This shows that the effect with the nonpolar liquids is not due to photooxidation. The vacuum irradiation produced a small decrease in the contact angle of poly(vinyl chloride) for water (about half that found in air irradiation) but no change in the contact angle for formamide or ethylene glycol, although the yellow color, characteristic of the formation of conjugated double bonds (16), was present. The effects shown in Fig. 4 for the polar liquids are thus primarily due to photooxidation. Both FMIR and transmittance spectra of the unirradiated polymer had bands in the carbonyl region at 1725 cm^{-1} and 1775 cm^{-1} (weak). These bands are not due to residual benzoyl peroxide or its decomposition products such as benzoic acid. The carbonyl absorption is probably due to the presence of oxidized poly(vinyl chloride) in the original polymer. It has been reported (17) that mechanical operations such as milling or grinding can bring about some oxidation of poly(vinyl chloride). Ultraviolet irradiation of the polymer increased the intensity of the carbonyl bands, showing that photooxidation occurred. No spectral evidence other than the yellow color observed visually was seen for the formation of unsaturated groups.

Poly(ethylene Terephthalate)

Like polystyrene, poly(ethylene terephthalate) is a strong absorber of ultraviolet radiation below 270 nm; the phenyl ring is the chromophore in both. However, their structures are considerably different, as shown in Table 3, and irradiation in air enhances the differences. In Fig. 5 are shown the contact angles for various liquids on poly(ethylene terephthalate) films which have been irradiated in air. The contact angles for hydrogen-bonding liquids initially decreased with irradiation time; thereafter the contact angles of water and probably ethylene glycol reached an apparently stable value. This might reflect a similarity between the degradation products and the polymer itself. The only change found in the FMIR spectrum of irradiated poly(ethylene terephthalate) was increased absorption in the O-H stretching region at 3350 cm^{-1}. Although poly(ethylene terephthalate) is regarded as a polymer which primarily crosslinks (18,19), at least under ionizing radiation, evidence has been reported (20) that in air radiation can bring about chain scission with the concomitant appearance of hydroxy and carbonyl groups apparently associated with chain ends. In the present work new carbonyl groups

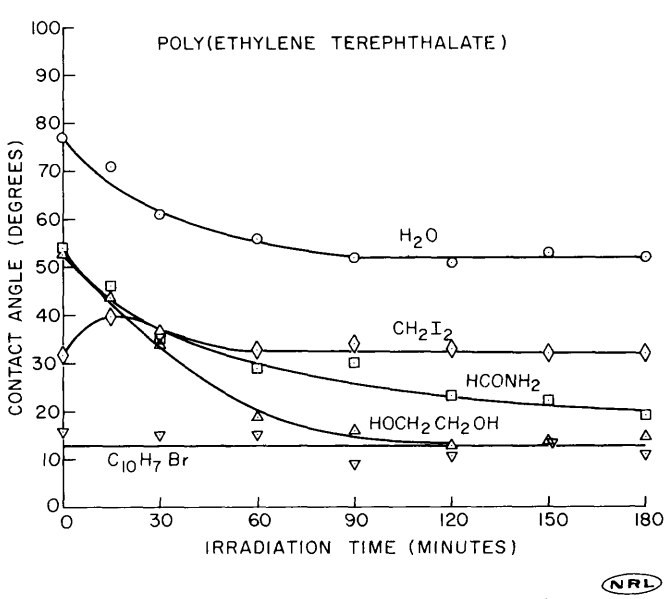


Fig. 5 - Changes in contact angles of various liquids on irradiated poly(ethylene terephthalate)

would be obscured by the carbonyl absorption of the ester linkage of the polymer. It seems entirely possible that the changes in the contact angles for the hydrogen-bonding liquids result from radiation effects (possibly crosslinking) that bring about a "disorientation" of the surface such that the ester oxygen atoms normally exposed in the surface (12) are displaced to some extent by carbonyl oxygen atoms of the ester linkage. Low-molecular-weight degradation products may play a relatively small role in the wettability changes. No change was found in the contact angle for 1-bromonaphthalene on poly(ethylene terephthalate) as a result of ultraviolet irradiation. The behavior of methylene iodide was unusual in that after an initial increase with irradiation time the contact angle decreased to the original value and remained constant thereafter. No explanation is offered for this behavior.

Poly(methyl Methacrylate)

Poly(methyl methacrylate) was investigated only briefly. Contact angles with the film after ultraviolet irradiation in air are shown in Fig. 6. After about 120 min irradiation it became impossible to obtain equilibrium contact angles for the hydrogen-bonding liquids, and initial contact angles were used in these cases. The contact angle of the nonpolar liquid 1-bromonaphthalene decreased slightly. The contact angle for n-hexadecane, however, increased to around 17° or 18°. Similar behavior was not found with any other polymer. The difficulty in obtaining equilibrium contact angles might be related to a rapid buildup of relatively low-molecular-weight polymer fragments on the surface of the irradiated poly(methyl methacrylate). It has been found (21) that this polymer undergoes rapid chain scission under ultraviolet irradiation both in air and in vacuum. Production of other low-molecular-weight photolysis products is apparently low (21), although it is likely that some oxidation products are formed. Extensive chain scission might affect the wettability of the polymer surface by roughening, or the low-molecular-weight fragments might be more soluble in some of the wetting liquids.

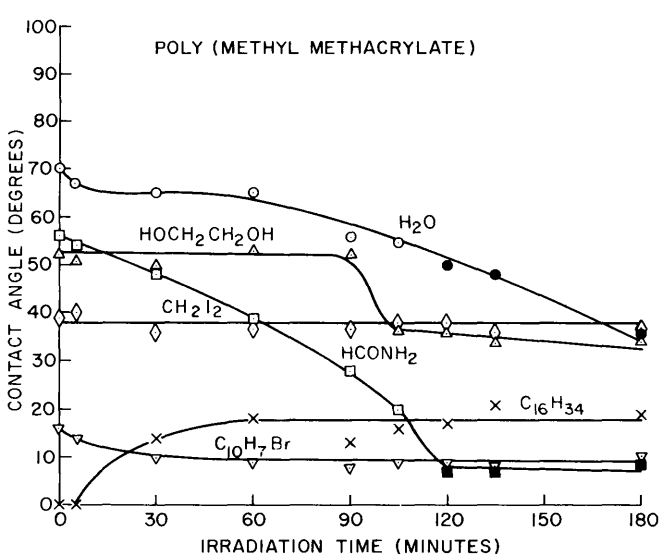


Fig. 6 - Changes in contact angles of various liquids on irradiated poly(methyl methacrylate). (Filled symbols indicate initial values.)

Poly(n-butyl Methacrylate)

Contact angle changes on poly(n-butyl methacrylate) as functions of irradiation time (Fig. 7) for the polar liquids were relatively small. As with the methyl ester, equilibrium contact angles were impossible to obtain after 60 min of irradiation for formamide and 120 min for water. No changes were seen in the contact angle of 1-bromonaphthalene. The changes must involve photooxidation, however, since irradiation in vacuum for 120 min resulted in no change in contact angles. Some broadening of the carbonyl bond (transmittance and FMIR spectra) occurred as a result of irradiation in air. However, the FMIR spectra of concentrated methanol and n-heptane extracts of irradiated films were virtually identical with the spectrum of poly(n-butyl methacrylate). Insufficient material was extracted by water to obtain an FMIR spectrum. Apparently the only extractable materials present were low-molecular-weight fragments of the polymer. It seems likely that the production of other low-molecular weight products is either low, or that the products are quite volatile. Although the photodegradations of poly(methyl methacrylate) and poly(n-butyl methacrylate) probably have much in common, the wettability changes (Figs. 6 and 7) are somewhat different. The relative lack of change in poly(n-butyl methacrylate) wettability with irradiation may reflect surface control by the aliphatic ester groups. Even though extensive main-chain degradative changes may be taking place in both polymethacrylates, lack of mobility may preclude penetration of the altered chains to the surface of the butyl ester; therefore the wettability of this polymer is comparatively unaffected by irradiation.

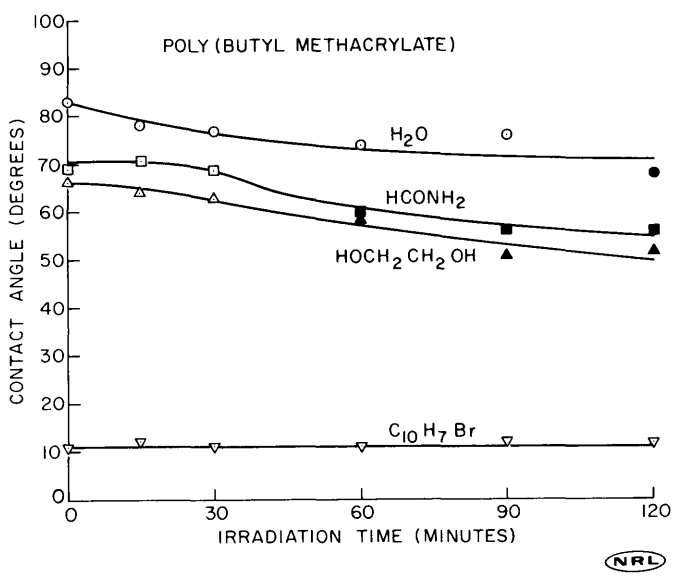


Fig. 7 - Changes in contact angles of various liquids on irradiated poly(butyl methacrylate). (Filled symbols indicate initial values.)

CONCLUSIONS

Changes in the wettability of a number of polymer surfaces during ultraviolet irradiation in air are an index of the photooxidation changes in these materials in the earliest stages of degradation. Specific changes in wettability are largely dependent on the chemical nature of the unirradiated and degraded surfaces; with a series of wetting liquids each polymer presents a unique sequence of wettability data during simulated weathering. This data can be related to chemical changes occurring during degradation. To the extent

that such chemical changes are harbingers of overt film failures, wettability measurements should prove to be a useful indicator of the life expectancy of organic-polymer-containing materials exposed to ultraviolet radiation in air.

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13. ABSTRACT

The effect of ultraviolet irradiation in air on the wettability of polymer surfaces by liquids of known surface tensions has been studied. The polymers studied were polystyrene, poly(vinyl chloride), poly(ethylene terephthalate), poly(methyl methacrylate), and poly(butyl methacrylate). Changes in contact angles of the contact liquids used were plotted versus the time of irradiation of the polymer surface. Spectral evidence is presented to show that photodegradation products include oxygenated moieties capable of interaction with polar liquids. Polymer fragments resulting from chain scission also play an important role in wettability changes for some polymers. Extraction and spectral studies of irradiated polystyrene surfaces showed that photodegradation products include small molecules, readily removed by extraction, and oxidized (as carbonyl) polymer chains which are not readily removed from the surface.

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Poly(vinyl chloride)						
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