

SERI/TP-334-571

CONF-800220--3

MASTER

REACTIONS AT THE SILVER/POLYMER
INTERFACE: A REVIEW

PAUL SCHISSEL
A.W. CZANDERNA

FEBRUARY 1980

PRESENTED AT THE SECOND SOLAR
REFLECTIVE MATERIALS WORKSHOP

HOLIDAY INN GOLDEN GATEWAY,
SAN FRANCISCO, CALIFORNIA
FEBRUARY 12-14, 1980

Solar Energy Research Institute

1536 Cole Boulevard
Golden, Colorado 80401

A Division of Midwest Research Institute

Prepared for the
U.S. Department of Energy
Contract No. EG-77-C-01-4042

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use or the results of such use of any information, apparatus, product, or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

REACTIONS AT THE SILVER/POLYMER INTERFACE: A REVIEW

Paul Schissel and A. W. Czanderna

Solar Energy Research Institute

Golden, Colorado 80401

ABSTRACT

One of the possible solutions for improving mirrors for long-life, inexpensive solar concentrators is to coat the reactive mirror material with a polymer. Polymer-coated reflectors may improve optical efficiency and reduce the cost of solar mirrors. Because the mirror/polymer interface may have long-term instabilities in a solar-stressed environment, it is necessary to isolate the effects attributable to the bulk materials from those of the interface. Actual failure mechanisms are unknown, but we present several possible explanations for failure of the polymer/mirror interface. The purpose of this paper is to review the literature on one of the systems of great current interest, the silver/polymer interface. First, the components of this interface are considered separately. Studies of reactions of environmental gases with silver are summarized. Then, several candidate fluoropolymers and polymethylmethacrylate are considered independently of the metal. The thermal, photo, and oxidative degradation reactions are briefly outlined. Finally, the limited data actually obtained on the silver/polymer interface are summarized. Results obtained on the silver/Teflon-FEP interface are emphasized because its use for thermal control panels in the space program resulted in extensive study.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

SECTION 1.0

INTRODUCTION

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

One of the major problems in concentrating solar radiation is to protect reflector surfaces so the reflectance will remain stable for ca. 20 years. Polymer-coated reflectors are one possible approach for protecting the metal from degradative surface reactions. The purpose of this review is to summarize the literature available to us on silver/candidate-polymer systems for solar applications.

Polymers are potentially cost-effective as overcoats for substrate mirrors. For the principal purpose of this paper, the direction of the incident radiation is not important; in fact, later in the report, the authors will favor using a superstrate (second-surface) mirror. If polymeric coatings could be made more reliable, the potential gains in ease of manufacture could lower costs. The technology has not advanced to the stage where a major commitment can be made to mirrors protected by polymers. For example, in arriving at their design for the Barstow pilot plant, McDonnell-Douglas [1] rejected acrylic, overcoat (first-surface) reflectors due to formation of pinholes, staining, and delamination. Acrylic coatings from several manufacturers were tested.

In contrast, the University of Minnesota/Honeywell [2] group has reported results on glazed parabolic concentrators. Tests at Phoenix, Arizona, showed negligible degradation of aluminum and silver mirrors protected by acrylic, Teflon, and glass after exposures exceeding two years. Accelerated exposure tests at Phoenix also gave negligible degradation. However, similar tests at St. Petersburg, Florida, and Minneapolis, Minnesota, were stopped because severe degradation in reflectance occurred in about one year. No explanation is given for the variations in these empirical tests of gross failures. However, they emphasize the importance of making more fundamental measure-

ments related to the degradation processes if we hope to be able to estimate life spans for these systems.

Macroscopic optical failures have also been reported from other effects than a gross failure. For highly concentrating systems, the reflected light should be specular to a high degree (engineering estimates suggest a tolerable error angle of 2 milliradians for one standard deviation for the most demanding conditions). Various degradation mechanisms can cause the scattering to become excessive. Probably the worst cause is simply the accumulation of dirt [3] on the mirror surface. Empirical tests of these scattering effects on transmittance and reflectance are leading to the compilation of a handbook for materials [4].

These empirical tests [4] include the effects of weathering, but no attempt is being made to correlate chemical change with optical degradation. To be useful for the design of high concentration systems, scattering data at small angles must be included and, at present, they are not. The characteristics of reflected beam profiles at small angles have been measured by Butler and Pettit [5,6] and Lind [7]. The data provide useful information for the design of concentrators.

Reports [8] of tests on protective layers of Teflon-FEP, Sheldahl proprietary acrylic coating, and other materials suggest that the accelerated test procedures are inadequate and that acrylic coatings show promise. In contrast, the summary report [8] states that none of the materials escaped degradation during a 6-month exposure and that acrylic appears less reliable than Teflon-FEP. Unfortunately, the data are not presented for independent analysis to resolve the apparent contradiction. The author [8] notes that the specular reflectance tests utilized an 8-milliradian exit angle. For any results to be of

meaningful use at large concentration ratios, the subtended incidence angles should be much less than 8 mrad.

Isakson [9] tested polymethylmethacrylate (PMMA) and polyvinylidene fluoride (VDF) modified with PMMA with accelerated weathering devices and by outdoor exposure. The 12.7- μm samples were coated on matte-finished, bright aluminum panels. Nine months exposure in Florida produced only minor band broadening in the IR spectrum for PMMA, while only 31 hours in a Dew Cycle Weatherometer totally obliterated the IR spectrum. Data for the VDF modified by PMMA showed that the PMMA portion was attacked more than the fluoropolymer.

A more recent summary [10] of solar reflective materials is available. Some of the materials considered for protecting solar mirrors have also been tested for protecting solar cells. A comprehensive review of the application to solar cells has been reported [11]. Experience with polymers in this application has been quite varied and delamination and moisture permeation have been major sources of failure [11]. Similarly, materials for space-flight application are potentially useful in solar applications. Silver-coated fluorinated polymers have performed well in space [12]. If problems relating to the ambient gases can be solved, these polymers might be used for mirrors.

Polymer-protected mirrors fail in several ways. Slow deterioration decreases the hemispherical reflectance and can lead to gross failure. These changes may decrease specular reflectance more rapidly than hemispherical reflectance. Color changes occur and retention dirt is increased. Pinholes form and expose the metal directly to the environment; delamination of the polymer from large portions of the mirror also exposes the metal. Attack may come from the mirror edges where a special sealing problem occurs.

Why these systems fail is mainly conjectural. To learn how to improve the systems, we need to express the failure modes in more fundamental terms. We know, in basic terms, how polymers fail. We do not know which of the basic failure modes is contributing to actual mirror failures.

In an attempt to connect the empirical tests with more fundamental measurements, let us consider some basic mechanisms which may be effective. All systems will face similar sets of stresses. The systems will operate at temperatures that will range between -30 and 55° C. In addition, they will be exposed to UV light, ambient gases, and the mechanical shocks of diurnal cycles. Mechanical stress during manufacture and installation may also be important. In practice many stresses will act simultaneously and, perhaps, synergistically, but for purposes of discussion they may be considered individually. Chemical changes due simply to thermal stress will probably not be a principal factor. Clearly, the systems will be chosen to be thermally stable in an obvious way; however, it is not obvious that any system is thermally stable in the long-term sense required for mirrors. Therefore, first we need to know and account for the basic thermolysis mechanisms. Then photolysis will probably be more important and is operative in several ways. Bulk stability of the polymer clearly is required, but the considerations and the caveat applied to thermolysis apply here also. Photolysis of the polymer-metal interface needs special consideration since little is known about how the metal affects the polymer. Photolysis can occur at the air-polymer interface where photooxidation by the ambient gases virtually always occurs. Oxygen is a chief offender; water vapor and specific pollutants will also have to be considered. Diffusion of gases through the bulk of the polymer must also be considered, and diffusion via imperfect edge seals directly along the interface may be more important.

Mechanical, photo, thermal, and atmospheric stresses could cause mirror failure in various ways. Degradation of the polymer, in some cases, produces low-molecular-weight fragments which could be formed in the bulk or at the metal surface. If these fragments accumulate at the interface, they could cause the delamination and pinholes. Alternatively, more direct attack on the bonding species could cause delamination. Non-chemical factors must be considered. The morphology of the polymer changes during crystallization at a metal interface. The stresses may interact with this transition zone without significant chemical change. If these conjectures are replaced by understanding, the procedures leading to better systems should become apparent.

The "same" polymeric material for a given system can vary. The catalysts used in preparing the polymer, the actual structures, tacticity, unreacted monomer, residual catalysts, and impurities all can alter the properties of the polymer. In general, our discussion uses information from the open literature, in which the materials are usually well characterized. Commercial materials may have a variety of additives which improve performance, the effects of which must be considered.

SERIO 



SECTION 2.0

OVERVIEW OF DEGRADATION MECHANISMS

Experience has shown that two metals and several polymers are candidates for glazed mirrors; silver, aluminum, polymethylmethacrylate (PMMA), polyvinylfluoride (VF), and fluorinated ethylene propylene copolymer (FEP). These materials are discussed and some additional candidates are noted in Table 1. Since all three polymers are relatively stable under UV, temperature, and weathering, why do mirrors fail? Some theories are postulated in this section.

2.1 THE AMBIENT GAS THEORY

The limitation for many applications of polymers may be the permeation by the ambient gases through the polymer, followed by attack at the metal interface. Alternatively, the gases attack the edge seals and then the interface via diffusion along the interface.

There is little doubt, for example, that water vapor can cause accelerated damage. It seems unlikely that simple diffusion through the bulk is the cause. Estimates of the permeation of water vapor through some unweathered polymers suggest that such long-term exposure from permeation would be less than that received during the time of fabrication in normal ambient atmospheres. We should not accept permeation data on virgin material as being representative but rather should seek alternative reasons for the permeation. Two alternatives have been documented. First, it has been observed that the permeability of Teflon-FEP can increase forty-fold during processing subsequent to manufacture [11]. For some polymers, weathering can cause surface microcracks which, as they propagate into the bulk, could increase permeability. Second, a complex synergism

between the effects of UV light and cycles of moisture and/or temperature has been observed [13]. Some questions could be answered by exposing mirrors to UV and heat in vacuum. Some answers have resulted from tests of materials for the space program [12]. Comparable data are not available for permeation through edge seals and along the interface [14].

2.2 THE MECHANICAL STRESS THEORY

There is a mismatch in the thermal expansion coefficients of the metals and polymers, possibly accentuated by some degradation from UV and/or ambient gases. Simple "sorting"-type experiments in which the stresses are applied one, two, or several at a time could answer certain questions. For example, do mirrors which are thermally cycled in the dark fail more rapidly than those maintained in the dark at the upper temperature? For some materials, such tests were carried out during the space program [12]. Thin silver films, vacuum-evaporated onto Teflon-FEP, were found to withstand thermal cycles in vacuum without UV radiation.

2.3 THE OUTGASSING THEORY

Interfacial delamination and/or reaction could occur by formation of volatile species at the interface or in the bulk, with subsequent concentration at the interface. The volatiles could be the products of thermal or photochemical reactions. In fact, in some systems which have been plagued with bubble formation and delamination, the problem appears to be due to thermal reaction of the adhesive. The adhesive is shielded from UV by

both the polymer and the metal mirror. These thermal reactions could be catalyzed by the metal.

2.4 THE UV-METAL THEORY

This theory assumes that the conjunction of polymer, metal, UV, and possibly the ambient, is required to induce a chemical change at the interface. If the sorting-type experiments suggest this is the case, the chemistry at the interface should be investigated, which prompts interest in analytical methods for surfaces, such as electron spectroscopy for chemical analysis (ESCA) and Fourier transform infrared spectroscopy (FTIR).

SERIO 

SECTION 3.0

REACTIONS OF SILVER WITH ENVIRONMENTAL GASES

The reactivity of silver with gases is important if environmental gases can permeate the polymer or if gases are formed by a UV-induced reaction of the polymer. The initial stage of gas/silver reaction requires adsorption of the gas onto the silver. Therefore, representative information from the literature about the interactions of oxygen, carbon dioxide, water, hydrogen, carbon monoxide, sulfur dioxide, nitrogen oxides, hydrogen sulfide, and hydrogen chloride with silver is discussed in this section. Silver is relatively inert to interaction with most gases until oxygen is adsorbed onto it, after which many gases will adsorb. For silver mirrors, it is likely that even a protected silver surface would have sufficient exposure to oxygen to produce the necessary precursor for adsorption of other gases.

There are substantial quantitative results on the equilibrium and rates of adsorption and desorption of oxygen on silver [15]. The most complete work was done on silver powders that had been treated to be clean and to give reproducible rates of adsorption and total uptakes of oxygen. Direct evidence shows that silver is not oxidized to a silver oxide in the temperature range of -78 to 400°C and with oxygen pressures up to 90.7 kPa [16]. More extensive measurements at 1.33 kPa and temperatures up to 350°C corroborate this conclusion [17]. Under these circumstances one monolayer of oxygen is the most that can be adsorbed. As has been noted [18], results of oxygen adsorption on $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ single crystals [19-21] lead to the same basic conclusions concerning the weak chemisorption of oxygen. At 3500 kPa (35 atm) of oxygen and 250°C , Ag_2O forms [17], but these extreme conditions are not encountered in solar applications.

If oxygen is available in a more reactive state, oxides do form. For example, silver subjected to a glow discharge in oxygen forms Ag_2O , while ozone forms higher oxides, possibly Ag_2O and AgO [22]. The presence of ozone or singlet oxygen could adversely affect silver for solar applications. Data on the reaction of singlet oxygen with silver have not been located.

The gases CO , CO_2 , H_2 , and H_2O do not react with clean silver (nitrogen atoms will interact but this is not important to solar applications [23]). However, if oxygen is first adsorbed on silver, these gases will interact. For example, CO_2 will adsorb on the dissociatively adsorbed oxygen on a one-for-one basis in the initial stages, presumably forming an $\text{Ag}\cdot\text{O}\cdot\text{CO}_2$ adsorbed complex. The CO_2 coverage is proportional to the oxygen coverage up to about half a monolayer of CO_2 [15,24]. At about 30°C and above 5.2 kPa of CO_2 , the coverage is insensitive to CO_2 pressure after at least half a monolayer of oxygen is adsorbed. At lower CO_2 pressures, or higher temperatures of the silver, carbon dioxide is weakly chemisorbed (E_D ranges from 84 to 100 kJ/mol) onto oxygen-covered silver and its presence promotes the desorption of molecularly adsorbed oxygen above $80\text{--}90^\circ\text{C}$ [25]. That CO_2 does not react with silver except as a chemisorbed species is corroborated by Auger measurements [26]. Water vapor will also adsorb on oxygen-covered silver at room temperature, but the available literature is not quantitative with respect to temperature and pressure dependence [15]. For solar applications, the absence of water vapor adsorption data is unfortunate since multilayer adsorption near room temperature is likely. The solution of acid-forming gases in this layer could result in serious corrosive attack.

Optical microscopy and transmittance data show that 52-nm films of silver on Pyrex start to agglomerate between 100 and 150°C [16]. At these temperatures, the agglomeration is retarded slightly by the presence of oxygen. (The well-known thermal etching at

temperatures above 500° C probably has a different mechanism.) The observed mobility of silver at such low temperatures combined with the excess free energy of a large thin silver surface layer suggests an unbacked mirror could fail under solar stressing because of the thermodynamic potential and favorable kinetic surface transport processes near the temperature of planned use. When oxygen is admitted to the clean film at 25° C, the transmittance decreases, which could result from the sensitivity of the optical constants to an adsorbed monolayer of oxygen.

Both hydrogen and carbon monoxide will remove oxygen from silver as water and carbon dioxide, respectively. Although most of the quantitative work reported was at temperatures between 300 and 400° C, cyclic reduction and reoxygenation has been carried out near 100° C on silver supported by glass wool [27]. After extensive outgassing, adsorption, outgassing, and reduction cycling on silver powder, both H₂ and CO reduced all but 0.1 monolayer of oxygen from the surface at room temperature [28]. Results of reduction reactions on <110> single crystals are similar to those obtained with powders [29].

The adsorption of sulfur dioxide on silver is even less studied than CO₂ and H₂O adsorption. Sulfur is removed as SO₂ and clean silver obtained in the early stages of cyclic oxygen adsorption and carbon monoxide reduction at 350° C [30]. One cycle was sufficient to oxidize the sulfur to a gaseous species at this temperature, but for solar applications the question of reactivity between sulfur and oxygen remains open. Furthermore, little quantitative information is available for the adsorption of SO₂ on oxygen-covered silver. Although Lassiter [26] was unable to detect oxygen on silver using AES (Auger Electron Spectroscopy) he did obtain a sulfur signal at low pressures of SO₂ and attributed this to sulfur. Barber et al. [31] used SIMS (Secondary Ion Mass Spectrometry) to show that both sulfur and oxygen are adsorbed when silver is exposed to 1.3 mPa of SO₂ or to mixtures of 10% SO₂ and 90% O₂ at the same total pressure. These authors suggest the

reaction is $\text{SO}_2(\text{g}) \rightarrow \text{SO}_2(\text{ads})$ followed by $2 \text{SO}_2(\text{ads}) \rightarrow \text{S}(\text{ads}) + \text{SO}_4(\text{ads})$. They also found sulfur is easily removed by heating in oxygen. (Sulfur films are also reported to be easily removed from copper and aluminum by oxygen at room temperature [32].) The difficulties in detecting AES signals by some researchers [20,26] have not been encountered by others [19,21]; the work by Heiland et al. [21] yielded excellent ISS (Ion Scattering Spectrometry) signals from adsorbed oxygen.

There is a dearth of information concerning the interaction of nitrogen oxides with oxygen-covered silver. A reasonable speculation, based on the interaction of NO and NO_2 with several oxide surfaces [33], is that NO and NO_2 would form a weak chemisorptive bond on oxygen adions.

The reaction $\text{Ag} + \text{H}_2\text{S} \rightleftharpoons \text{Ag-S}(\text{ads}) + \text{H}_2$ has been studied at high temperatures with radioactive tracers and detailed isotherms have been obtained [34]. Adsorbed sulfur enhances the surface mobility of silver [35]. It is more difficult to remove adsorbed sulfur with $\text{H}_2(\text{g})$ than with $\text{O}_2(\text{g})$ [36]. The rate of formation of Ag_2S from room air varied from 0.5 to 2 nm per week, presumably depending on the impurity of the air [37]. Other measurements of tarnish in air (tarnish is usually Ag_2S) show rates from 0.1 nm/h up to 6 nm or more in one month. There is no tarnish in dry N_2 , while rates of 10 nm/h are obtained in a humid atmosphere containing 10% H_2S [38]. At tarnish thicknesses of about 6 nm, the rate of tarnish decreases; however, at thickness of about 16 nm, needle formation occurs and the growth rate suddenly increases. Presumably, H_2S reacts with silver at low temperatures only in the presence of both oxygen and water vapor [39], and halogens can inhibit the formation of Ag_2S [40].

The salt-containing vapor of artificial sea water did not visibly attack a silver surface [41]. Low levels of chlorine impurities in silver powder can be purified by a

hydrogen reduction reaction at temperatures greater than 300°C, which results in evolving HCl [17,36]. Alternatively, the reaction between silver and chloride-bearing gases has been used frequently to inhibit the reactivity of silver surfaces to other gases, especially when used for the catalytic epoxidation of ethylene to ethylene oxide on silver [42]. At the temperature used for this reaction, the reaction between silver and pure ethylene dichloride is very rapid (many monolayers per hour). The rate of reaction at room temperature is much slower and the silver surface adsorbs less oxygen, which presumably is in the molecular form required for a good catalyst. It is hypothesized that oxygen adion sites are occupied by chloride ions. This established catalytic reaction mechanism [42] is of considerable possible value for passivating solar mirrors. If oxygen-bearing gases (H₂O, SO₂, CO₂, NO₂, etc.) adsorb on the oxygen adions on a silver surface and these sites can be eliminated by the proper amount of adsorbed chlorine, then pretreatment with adsorbed chlorine might passivate the silver surface against corrosive reaction by oxygen-bearing gases. A more systematic appraisal of these reactions could influence the polymer selection; for example, if the primary pollutant is SO₂, enhanced permeability of oxygen relative to SO₂ might retard Ag₂S formation. If the pollutant is primarily H₂S, the results quoted in the literature suggest that reducing the quantities of H₂O, O₂ or H₂S will decrease the tarnish. Alternatively, surface treatments with halogens could passivate the surface against both sources of sulfur. For example, the oxygen remaining on the silver surface might not be of the proper form to permit the formation of Ag₂S from an H₂S ambient.

The reaction of seriously degraded coated (first-surface) silver mirrors with sulfur, chlorine, and oxygen has been reported [43]. The products were identified using ESCA, ISS, AES and SIMS. Visually clear regions contained silver to a depth of over 50 nm, while copious amounts of sulfur and oxygen were identified on visually reflecting regions

of the same mirrors. Shifts in the ESCA peaks for sulfur indicate partially oxidized sulfur but the +6 state in the sulfate radical was not attained.

In summary, oxygen readily adsorbs on silver at room temperature, and atmospheric and pollutant gases, such as H_2O , CO_2 , CO , SO_2 , and NO_2 , adsorb on the oxygen-covered silver. At the conditions of solar stressing, formation of bulk silver oxide compounds is unlikely but formation of bulk silver sulfide, silver chloride, and silver oxysulfur compounds is probable when silver is exposed to appropriate gases. The literature available is inadequate for deducing the potential compound-forming reactions by several gases co-chemisorbed onto silver.

SECTION 4.0

REACTIONS OF CANDIDATE POLYMERS WITH ENVIRONMENTAL GASES

4.1 FLUORINATED POLYMERS

If thermal stability were the only criterion, many polymers would be acceptable. Theoretically, many polymers are transparent to visible and solar UV light, particularly in thin films. They should be optically acceptable and resistant to UV degradation. In fact, many are prone to UV degradation, which may be due to secondary factors. For example, oxygen can form charge-transfer complexes with some polymers which then permit adsorption of radiation up to 340 nm [44,45]. An extreme example is polyethylene, which degrades badly when unprotected. At the other extreme is PMMA, which degrades very slowly. Most materials performing well as mirror glazes owe their protection to their transparency to UV.

In general, the fluorocarbon polymers are of interest because they are chemically inert, have excellent resistance to UV, are thermally stable, and have excellent weatherability. Thin films of fluorocarbons are transparent but their optical qualities in general are not quite as good as those for PMMA. Unfortunately, in a recent excellent review of the photolysis of polymers [46], the photolysis of fluorinated polyethylenes is not mentioned. A summary of synthesis methods is available [47]. A summary [11] of the materials, their properties, and their application for encapsulating solar cells is the basis for this section. In Table 1, the entire family of commercial fluorocarbons is listed. Only polytetrafluoroethylene (TFE) is processed by sintering methods. The other materials are processed by more conventional means but still at relatively high temperatures. Very little scientific evaluation of these materials is available so that a coherent presentation is possible only for thermolysis. However, a brief summary of the available information

for each material is worthwhile. Although TFE is not of direct interest because of the present difficulty of processing, a data summary is included as a guide to the behavior of the other materials.

In contrast to the dearth of scientific papers, there is considerable practical literature, particularly regarding encapsulating solar cells [11]. Because these materials have such outstanding qualities, the emphasis has been on the processing and particularly the bonding of the materials to substrates. This is discussed in subsequent sections on interfaces.

4.1.1 TFE

Among the fluorinated ethylene polymers, TFE is unique in that, when heated in vacuum to about 450°C, it unzips to yield 96% monomer with an activation energy of 339 kJ/mol [48,49]. The other members of this family preferentially eliminate hydrogen fluoride under similar conditions. Degradation is first order over the entire temperature range with no evidence for any marked change in activation energy during conversion [49,50]. Several studies have shown that the material is stable under thermolysis [51-54]. When TFE is thermalized in an ambient of monomer and gaseous pyrolysis products, the thermolysis rate is decreased and the product distribution altered; C₃F₈ is dominant and the quantities of C₂F₄ and C₃F₆ are equal and half of the C₃F₈ content [49]. (This may be more representative of the mirror interface).

Heating TFE in air at 400 to 450°C did not change the subsequent rate of thermolysis in vacuum. At 470°C the rate increased slightly [55]. Thus, TFE has a similar thermal stability in oxygen and in vacuum [46]. A comparison of the reactivity of TFE and several other materials with oxygen atoms (Table 2) shows rather small variability in the rates

of reaction [56]. These reactions took place at 40 to 70° C and were limited to the surface; the bulk was unchanged. Other studies of oxidative thermal stability have been reported [57a]. TFE reacts with ozone to produce perfluoroformaldehyde and CO₂ while, surprisingly, polyethylene is relatively unreactive [57b].

Photooxidation results are meager, presumably because the material is "almost totally resistant to photooxidation" [48]. The photoinduced thermal decomposition of TFE has been given a cursory examination. It showed "only a feeble though definite response to the UV light used" (a medium-pressure quartz mercury lamp) [58].

Gamma radiation in air greatly accelerates the rate of scission [59]. "Exposure to various gases during radiolysis profoundly alters the EPR spectrum. It has been suggested that radiation damage is altered by these gases" [48]. It would be of interest to see if UV has similar effects. Radical formation by irradiation by x-rays and the subsequent reaction of the centers with oxygen have been observed [60].

4.1.2 CTFE

CTFE has somewhat less thermal stability than TFE. For example, a sample (molecular weight 100,000) was prepared without catalyst and was formed into a 0.2-mm sheet. Thermolysis in vacuum yielded about 27% monomer and some C₃F₅Cl and C₃F₄Cl₂ [61,62]. The activation energy was 238.5 kJ/mol [48,63]. The involatile residue was a transparent glass. When pyrolyzed in bulk or in the presence of N₂, the yield of monomer was much higher (67%). Thermal oxidation studies have been reported [64]. CTFE is essentially as thermally stable in oxygen as it is in vacuum [46].

CTFE also is "essentially totally resistant to photooxidation" [48]. It "is stable to UV, and only at high temperatures (250°C) degradations occur" [65]. Photoinduced thermal decomposition was carried out about 100°C below the temperatures of the straight thermolysis studies [58]. These qualitative experiments showed that the addition of UV from a medium-pressure quartz mercury lamp increased the decomposition rate to monomer (time constant of ca. 30 minutes). Upon turning off the lamp, the decomposition rate decayed slowly (time constant of ca. 30 minutes). Arguments were presented to show that the decay is a measure of intermediate radicals which, in fact, decay bimolecularly. Radical formation by irradiation by x-rays has been observed [60].

CTFE has outstanding barrier characteristics to gases and especially water vapor; it has the lowest transmission rate of water vapor of any transparent plastic film [66]. Unlike other fluorocarbons, it is optically clear in 1/8"-thick sections [66].

4.1.3 VF

Wall and coworkers have studied the pyrolysis of VF in vacuum [67,55]. Their data cover only a small temperature range near 373°C, where the weight loss was relatively rapid (ca. 1% per minute). They measured an activation energy of 230 kJ/mol. The data were obtained using 0.1mm Tedlar film. The principal products are hydrogen fluoride and some benzene. Complete pyrolysis left 5% char, which the authors interpreted to be due to thermally induced crosslinking. Prior irradiation with gamma rays greatly increased the pyrolysis rates.

VF has less thermal stability in air than in vacuum, in contrast to TFE and CTFE [46]. The reaction with oxygen atoms was noted in Table 2. Photodegradation of

polyvinylchloride (VC) proceeds by loss of HCl, similar to its thermal degradation [48]. VF may do the same, however, data have not yet been located. Radical formation by x-rays is observed [60].

4.1.4 Polyvinylidene Fluoride (VDF)

Madorsky [68] studied a material which had been polymerized by gamma rays and was, therefore, highly crosslinked. It was a hard, white, rubbery material and may not have the requisite optical properties. The same doubt applies to several copolymers containing VDF whose thermolysis was measured [58]. Recently, during program reviews, it was reported that films of biaxially oriented material have good optical properties. Optical and weathering tests are in progress. The thermolysis proceeds with an activation energy of 201 kJ/mol and at completion leaves a carbonaceous residue which is easily pulverized. Wall et al. [67] performed similar experiments using a commercial, milk-white powder (Kynar), which was pressed into a 0.25- to 0.3-mm film (pressing for 30 seconds at 242°C). The principal product is hydrogen fluoride, with less benzene produced than from VF. Pyrolysis to completion at 410°C left 30-35% char and indicated that VDF is somewhat more stable than VF. The authors note that prior irradiation with gamma rays greatly increased the pyrolysis rate but confirmed the value for the activation energy of 201 kJ/mol. It is interesting that crosslinking does not necessarily mean enhanced pyrolytic stability [67]. Although probably adequate, the thermal stability in oxygen is less than in vacuum [46]. A reaction between VDF and aluminum has been noted [69].

4.1.5 FEP

Pyrolysis of FEP results principally in the two structural monomers, with somewhat less total monomer yield than from TFE [58,70]. Initially, the relative amounts are 85% C_3F_6 and 9% C_2F_4 , while near the end of the degradation process the amounts are 19% C_3F_6 and 68% C_2F_4 . This suggests that FEP is about 80% TFE. The rates have a dual character. The initial rapid volatilization, corresponding principally to loss of C_3F_6 , is followed by a much slower rate of volatilization similar to the rate for TFE. FEP has a much lower activation energy (230 kJ/mol) than TFE (339 kJ/mol), but compensating pre-exponential factors (FEP, $10^{12} s^{-1}$; TFE, $10^{19} s^{-1}$) result in thermal rates which are not greatly different at the temperatures of the experiments.

It has been demonstrated that FEP can be vacuum deposited by thermolysis to form thin, colorless, transparent films [71]. In contrast, films of TFE cannot be made by this process; TFE films formed by r.f. sputtering are colored. While FEP is less stable in oxygen than it is in vacuum, the rate of weight-loss is probably slow enough for 20-year lifetimes. FEP undergoes scission and crosslinking during UV irradiation [65,72].

4.1.6 PFA, E-TFE, E-CTFE, Polytrifluoroethylene (TriFE), and Poly (1, 1-dichloro-2, 2-difluoroethylene) (DCDFE)

Data on the degradation of Teflon-PFA were not found. Some tests have shown darkening with use as covers for solar cells and moderate loss of transmittance with accelerated weathering [73]. E-TFE becomes gold colored upon exposure to UV [12]. It showed moderate transmittance loss with weathering and accelerated weathering [73]. For E-CTFE, weathering tests have been reported [74]. TriFE is not a commercial material.

Like VF, TriFE volatilizes to form hydrogen fluoride. DCDFE is not a commercial material either, but it may offer an optimum combination [75]. It appears that adding fluorine to polyethylene increases UV and oxidative stability while adding chlorine to polyethylene decreases permeability.

Comparisons are available regarding the thermal stability of a number of polymers [55,61,68]. The data show the percentage of sample volatilized by maintaining the sample at successively higher temperatures for thirty minutes. There are several interesting generalities. There are two types of materials, those with 100% volatility and those that form an involatile char. TFE is the most stable, but many materials would be sufficiently stable if the only stress were thermal. In Table 3 values from the published data are presented for the temperature at which 50% weight-loss occurs in 30 minutes. The relative stabilities are, in general, not sensitive to temperature. Additional data on non-commercial polymers are available [46].

4.2 POLYMETHYLMETHACRYLATE (PMMA)

PMMA is colorless and has solar transmittance of 82-85% for thin films, good dimensional stability, and excellent resistance to outdoor weathering. Water absorption has little effect on its optical qualities. Thermolysis of PMMA in an oxygen-free environment proceeds almost exclusively by sequential elimination of monomer units (i.e., 95% monomer yield) [76]. Madorsky [77] pyrolyzed two PMMA samples: sample A (molecular weight 150,000) was made using benzoyl peroxide as promoter; sample B (molecular weight 5,100,000) was made without a promoter. Sample A (0.6% residual benzoyl peroxide) was pyrolyzed at 240-270°C (138 kJ/mol), while B required temperatures of 310-325°C (230 kJ/mol). When A was preheated and then pyrolyzed, it behaved like B. The

author concluded that the difference in behavior was not due to the difference in molecular weight. Rather, it appears that benzoyl peroxide acts also as a catalyst for decomposition. More recent work shows that "low-molecular-weight PMMA has a more complex pattern of degradation than those of high molecular weight because of the much increased importance of chain-end initiated depolymerization" [78,79]. This difference is correlated to the mode of polymerization [46]. PMMA can be destabilized by chlorine radicals (from polyvinylchloride) [80,81] and by acetate ($\text{CH}_3\text{COO}^\cdot$) radicals from polyvinylacetate [82] or silver acetate [80]. Jellinek [83] found little difference in the activation energy (259.4 to 284.5 kJ/mol) for thermal degradation of the isotactic, syndiotactic, and atactic forms, although the syndiotactic form was somewhat more stable. Madorsky [63] has discussed the discrepancies in the values of activation energies.

Ranby and Rabek [65], Geuskens [46], and Gupta [84] have discussed the photolysis of PMMA and have provided the basis for our summary. The ultraviolet absorption spectrum of PMMA indicates that essentially no photolysis should occur under AM1 illumination. Empirical tests on PMMA, alone and with mirrors, verify this conjecture [85]. Long-term, subtle effects lead to failure. To accentuate the photolysis, most laboratory experiments have used shorter wavelength radiation (usually 253.7 nm), where absorption is still low enough to allow penetration of the bulk of the polymer. As Gupta [84] has emphasized, care must be exercised in using such data to estimate the behavior of PMMA at AM1 conditions. PMMA, if not unique, is unusual among polyalkylacrylates in that crosslinking does not occur during photolysis of films in air [86]. PMMA is unusual also in that the number of chain scissions per molecule tend to be linear with irradiation time [86].

Fox and coworkers [87,88] observed the principal products methylformate, methanol, and methylmethacrylate with quantum yields of 0.14, 0.48, and 0.2, respectively, from photolysis in vacuum. Photolysis in air yields the same species and also methane, hydrogen, carbon monoxide, and carbon dioxide. Allison [89] observed that the low-molecular-weight fragments were chiefly carbon monoxide, methylformate, and methanol when photolysis was in vacuum. These occurred in a ratio of 3, 6, and 10 molecules, respectively, per chain scission. Ackerman [90] photolyzed thin films of PMMA in oxygen and observed the products methanol, formaldehyde, methylacetate, methylformate, water, formic acid, carbon dioxide, and methane. Methylmethacrylate can occur from chain unzipping or unreacted monomer, which could account for variability of results.

Gas is formed during high-energy irradiation of PMMA. When the internal pressure of the gas formed in the reaction is sufficient to overcome the viscosity of the irradiated polymer, bubbling occurs. By suitable control of the irradiation dose and subsequent heating of the polymer, this bubbling effect can transform PMMA into a foamed material [46].

ESR spectra of PMMA irradiated with UV and gamma rays are almost identical [65] while the structures of the radicals, which are formed, are controversial. Some evidence suggests that radical formation is related to unreacted monomer [91].

Spectral changes have been observed during photolysis when the polymer yellows. It has been suggested that yellowing is due to formation of conjugated double bonds [89] and that carbonyls are also formed [92]. These new species produce chromophores at 240 nm and 285 nm, respectively, which could cause the onset of more rapid photodegradation.

A rather complete, plausible reaction scheme can be devised for the photolysis [65,46,84]. It is based on the radicals formed, the changes in optical spectra, and the volatile products. Use of these data as they apply directly to mirror failures is much more difficult. For the present we note the major points. With the exception of hydrogen, at low temperatures all of the gaseous products have been shown to originate from the ester side chain, probably via formation of $\cdot\text{COOCH}_3$. As the temperature is increased, depropagation becomes important and yields monomer as an additional gaseous product. The degradation produces new chromophores which are incorporated in the degraded polymer and not in the volatile products.

Price and Fox [93] have studied the surface reactions of several polymers under UV irradiation in air. Their criterion for reaction was wettability, determined with liquids of known surface tension. Wettability is also influenced by changes in crystallinity [94] and other factors [93], so actual structural changes are somewhat conjectural. Fox [88] et al. observed chain scission in PMMA to be the dominant reaction due to UV, both in vacuum and in air. This led them to conjecture that the accumulation of low-molecular-weight fragments on the surface altered wettability, with surface oxidation being a secondary factor. Their observations relate to the polymer-air interface and may not be directly applicable, but this mechanism could also operate at the polymer-metal interface and contribute to delamination.

Permeability may be more significant for PMMA than for the fluorocarbons. Rosen suggests stress-strain mechanisms from a penetrant lead to enhanced permeation via microfractures [95,96]. He specifically notes that stresses on unsupported PMMA enhance permeation even though microscopic stress cracks are not visible. Similar phenomena of stress-increased permeation have been measured for Pyrex glass. It is quite interesting that a Mylar which is craze-resistant did not show stress-increased permeation.

The diffusion of oxygen in PMMA which has been irradiated with gamma rays or electrons is also stress related. Barker [97] has used an optical method to measure the diffusion coefficient of oxygen in PMMA and to note its variation with stress. In regions of tensile stress, diffusion is enhanced; it is retarded under compressive stress.

Bueche [98] measured the diffusion coefficient of water vapor for PMMA by comparing the rate of weight gain to the equilibrium value of weight gain for thin polymer films. He noted the anomaly that sorption and desorption yield different values for the diffusion coefficient. He relates these results to permeability and calculates a value of 5.2×10^{-8} g cm cm⁻² hr⁻¹ torr⁻¹ at 25° C. He states that this value is in reasonable agreement with unpublished, direct permeability measurements made at the Rohm and Haas Co. His result is higher than other published data [99].

Practical tests of PMMA have included thermal, UV, and weathering stresses over seventeen years of outdoor exposure in New Mexico [85]. The samples were mounted 45° to the horizontal, facing south. The principal optical degradation, due to surface abrasion, amounted to 10%. Thus, research on abrasion-resistant coatings is clearly needed. The researchers further observed that the bulk transmittance losses (3%) increased progressing from the back to the front surface of the samples.

Clark and Thomas [100] analyzed a series of polymethacrylates, including PMMA, and established a basis for further ESCA measurements. As the authors point out, these are relatively difficult materials to analyze with ESCA. The spectrum for the carbon 1s level shows the carbon with the double-bonded oxygen clearly separated from the remaining carbons and the carbon with the singly-bonded oxygen appears as a shoulder on the major carbon line (i.e., the line corresponding to carbons with no oxygens attached). Deconvolution techniques allow these three carbon types to be isolated. The oxygen 1s

signal also shows doublet character corresponding to the two types of oxygen bonding. A more refined analysis of all the differently situated carbons is not possible. From more detailed spectral analyses, the authors conclude the samples have carbon/oxygen compositions corresponding to that expected from model compounds. They further conclude that the samples are homogeneous to the surface as defined by ESCA escape depths. There is no preferential ordering of alkyl groups at the surface.

SECTION 5.0

THE SILVER-POLYMER INTERFACE

5.1 SILVER-FLUORINATED POLYMER

Empirical experience with this system is extensive. The most pertinent work was done for NASA on silver-FEP coatings for space applications [12]. This work provides valuable information which could be used in developing silver-FEP mirrors. The goal for space applications was to develop the thermal coating with appropriate adhesive and to scale-up laboratory procedures to attain reproducible manufacture in quantities to coat 148.6 m² per space flight. The basic configuration consists of 0.127 mm Teflon FEP vacuum-coated with 125 nm of silver over which a 25-nm protective coating of Inconel 600 is deposited. This unit is attached to the main frame of the spacecraft with double-sided adhesive tape.

The FEP-Ag interface has good adhesion during thermal cycling in vacuum, but thick silver films may have poorer adhesion [101]. An earlier report summarizes methods of bonding fluorocarbons [102]. It is noted that the peel strength between FEP and a silicon solar cell was reduced by short-term exposure to high humidity and temperature [103]. Additional exposure caused delamination, which was attributed to water vapor permeation. The authors indicated that the heat sealing process can increase the water vapor permeability of FEP forty-fold [103]. A more systematic approach to the delamination problem showed that water vapor was just as effective a delaminating agent for the FEP-Ag interface as was the vapor over artificial sea water (N₂ was bubbled through the "sea water" to ensure dissolved salt entered the vapor). The data indicate that delamination is very sensitive to the relative humidity, and that the time until initiation of

delamination increases as the water vapor content decreases. The same tests indicate that the Mylar-Al interface was not affected [41].

Enhanced initial adhesion may retard attack by water vapor. Methods developed to improve adhesion between FEP and gold may be emulated for silver. These include chemical treatment [104], sputtering [105], crosslinking by activated species of inert gases [106,107], and electron irradiation [108]. Some evidence suggests that formation of a thin, oxygen-containing layer on FEP increases the adhesion. One procedure creates this layer by first vaporizing aluminum onto FEP and then dissolving it off with sodium hydroxide. Electron spectroscopy shows that the aluminum reacts with the fluorine in FEP and both are removed during the dissolution, at which time the oxygen-containing film forms. In other adhesion studies, Bhasin [109] plasma-polymerized TFE (PPTFE) onto 304 stainless steel, Al, and Ag. Peel strengths were 107, 107, 111 kg cm⁻², respectively. Peel strengths were independent of the type of metal and failure occurred in the polymer film. Variable amounts of polymer were left on the metals. Invisible residual polymer was revealed by ESCA. PPCTFE (plasma-polymerized chlorotrifluoroethylene) behaved very differently. Peel strengths were 94 ± 21, 72, and 181 kg cm⁻² for 304 stainless steel, Al and Ag, respectively, and residual polymer was never visible. While the rupture apparently was always near the interface, ESCA again showed that fluorine and chlorine were transferred to the metals. It is interesting that PPCTFE, in contrast to CTFE, has low molecular weight (1300-1600), is not highly crosslinked, and is relatively soluble.

The fundamental limitation of polymers may be their permeability to ambient gases. The least permeable polymers are more permeable than glass by several factors of ten [110].

Some tests have indicated that permeation of water vapor through FEP structures may be more dependent on the quality of edge seals and interface adhesion than on bulk permeation [14a]. The FEP-Ag-Inconel units developed black spots on the silver during storage periods of about one year. This occurred without elevated temperatures or UV light. Accelerated testing using atmospheres enriched with H₂S showed very rapid degradation of the silver. The metallized coatings (Ag and Inconel) had pinholes so the mode of attack was not proven to be permeation through the FEP.

Several studies have shown that FEP, in vacuum, is stable under UV irradiation [101]. Real-time exposures of 15 years in Florida have not altered the transmittance of FEP films [111]. The FEP-Ag interface is also stable under vacuum conditions (exposure rate of five suns for 600 equivalent sun hours) [112]. However, when irradiated in an ambient of oxygen, a large decrease in reflectance occurs [112]. More experiments are needed to determine if this failure is due to a reaction at the interface.

Teflon-TFE has been tested as a high-temperature insulator for silver and silver alloy electrical conductors [113]. Environmental tests included high-temperature salt spray, temperature cycles, and humidity. In each of these tests the insulation remained intact. In each test the surface of the wire showed slight tarnish which was insignificant for electrical applications but which may be detrimental for mirrors. During a water immersion test, the TFE-Ag wire developed non-metallic black spots; during temperature cycling the TFE-silver alloy did the same. The spots were scattered over the entire length of the wire surface. The bulk of the wire was not corroded and the insulation was intact. From these experiments, it seems that the bond between TFE and Ag is weak and may result in a "capillary-type" penetration along the interface.

Silver and copper have been observed to be incompatible even when separated by thin films of nickel. The result is an electrochemical corrosion so common as to be named "Red Plaque". Small openings in the nickel (and silver) are points of failure, possibly similar to the pinholes found in the H₂S tests on FEP-Ag mentioned above [113]. Carbon black [114], sintered metals (Au,Ni), and metal blacks (Au,Pt) are observed to increase the degradation, and decrease the melt viscosity of TFE [115]. The high surface area and, possibly, catalytic effects enhance degradation. Large surface areas for the Ag-polymer interface may be a means of accelerated testing for reactions at mirror surfaces.

5.2 SILVER-PMMA

Data relating specifically to this interface as used in mirrors has not been located, possibly because PMMA provides insufficient protection. The earlier discussions suggest possible failure modes. The long-term outdoor exposure tests demonstrate the stability of the polymer [85], but the long-term stability of the silver and of the polymer in the presence of silver is unknown. The thermal and photochemical degradation does produce volatile species which may preferentially accumulate at the interface [116]. Silver may catalyze reactions of the polymer analogous to the copper-catalyzed oxidation of polyethylene [117]. PMMA is destabilized by chlorine radicals [80,81], and by acetate radicals [82] from silver acetate [80]. Methyl acetate is observed during the decomposition of PMMA in air [90]. Perhaps a reaction at the interface due to concentration of acetate radicals is enhanced by the silver.

REFERENCES

- [1] McDonnell-Douglas Astronautics Co.-West, Central Receiver Solar Thermal Power System, Phase 1, Vol. III (Book 1, Collector Subsystem), Preliminary Draft, MDCG 6776 (May 1977).
- [2] University of Minnesota and Honeywell, Research Applied to Solar Thermal Power Systems, NSF/RANN/SE/GI-34871/PR/74/4 (January 1975).
- [3] R. S. Berg, A Survey of Mirror-Dust Interactions, ERDA Concentrating Solar Collector Conf., Georgia Inst. of Tech. (Sept. 26-28, 1977).
- [4] J. E. Gilligan et al., Polymer Chemistry Section, Illinois Institute of Technology Research Institute, ERDA EY-76-C-02-0578-034, *0002 (IITRI, Jan. 1978).
- [5] R. B. Pettit, Solar Energy 19 (1977), 733.
- [6] a. B. L. Butler and R. B. Pettit, Proc. of Soc. Photo-Optical Instrumentation Engineers, San Diego, CA (Aug. 24, 1977).
b. R. B. Pettit and B. L. Butler, ERDA Concentrating Solar Collector Conf., Georgia Inst. of Tech. (Sept. 26-28, 1977), SAND-77-1466.
- [7] M. A. Lind, J. S. Hartman, and H. L. Hampton, Proc. of the Photo-Optical Inst. Eng. 161 (1978) 98.

- [8] W. M. Arden, Reflective Materials Evaluation, Final Report, Task III, July 1975-April 1977, ERDA EY-76-C-02-2699 (Sheldahl, Inc, Northfield, MN).
- [9] K. E. Isakson, J. of Paint Technology 44 (1972) 41.
- [10] M. A. Lind and L. E. Ault, Summary Report of the Solar Reflective Materials Technology Workshop (Oct. 1978), PNL-2763.
- [11] D. C. Carmichael et al., Review of World Experience and Properties of Materials for Encapsulation of Terrestrial Solar Arrays, Final Report, ERDA/JPL-954328-76/4 (Battelle Columbus Lab., July 21, 1976).
- [12] N. W. Reed, Silver-Teflon Coating Improvement, Report #T169-71, Contract NAS9-10534 (Vought Corp., Dallas, TX, Dec. 23, 1976).
- [13] A. Blaga and R. S. Yamasaki, J. Mater. Sci. 11 (1976) 1513.
- [14] a. D. C. Carmichael, Studies of Encapsulation Materials for Terrestrial Photovoltaic Arrays, 5th Quarterly Progress Report, ERDA/JPL-954328-7616 (Battelle Columbus Lab., Dec. 27, 1976).
- b. D. C. Carmichael et al., Evaluation of Available Encapsulation Materials for Low-Cost Long-Life Silicon Photovoltaic Arrays, DOE/JPL-954328-78/2 (Battelle Columbus Lab., June 30, 1978).

- [15] A. W. Czanderna, in: *Microweighing in Vacuum and Controlled Environments*, ed. A. W. Czanderna and S. P. Wolsky (Elsevier, Amsterdam, 1980) p. 175.
- [16] a. A. W. Czanderna, *Vacuum Microbalance Techniques*, Vol. 5, ed. K. Behrndt (Plenum Press, New York, 1966] p. 135.
- b. J. S. Hammond et al., *Anal. Chem.* 47 (1975) 2193.
- [17] A. W. Czanderna, *J. Phys. Chem.* 68 (1964) 2765.
- [18] A. W. Czanderna, *J. Vac. Sci. Tech.* 14 (1977) 408.
- [19] G. Rovida, F. Pratesi, M. Maglieha, and E. Ferroni, *Surface Sci.*, 43 (1974) 230.
- [20] H. A. Engelhardt and D. Menzel, *Surface Sci.*, 57 (1976) 591.
- [21] W. Heiland, F. Iberl, and E. Taglauer, *Surface Sci.*, 53 (1975) 383.
- [22] A. Butts and C. D. Coxe (eds.) *Silver: Economics, Metallurgy, and Use*, (Van Nostrand, Princeton, N.J., 1967).
- [23] G. H. Cosma, *Thin Solid Films* 13 (1972) 185.
- [24] A. W. Czanderna, *J. Colloid and Interface Sci.* 22 (1966) 482.

- [25] A. W. Czanderna, and J. R. Biegen, *J. Vac. Sci. and Tech.* 8 (1971) 594.
- [26] W. S. Lassiter, *J. Phys. Chem.* 76 (1972) 1289.
- [27] G. W. Keulks and J. F. Outlow, *Proc. 5th Intern. Conf. Cat.* 2 (1972) 959.
- [28] A. W. Czanderna, unpublished.
- [29] H. A. Engelhardt, A. M. Bradshaw, and D. Menzel, *Surf. Sci.* 40 (1973) 4.
- [30] A. W. Czanderna, *J. Phys. Chem.* 70 (1966) 2120.
- [31] M. Barber et al., *Chem. Phys. Lett.* 27 (1974) 436.
- [32] D. H. Buckley, *NASA Tech. Rept.* D7340.
- [33] A. W. Czanderna and R. Vasofsky, *Prog. Surf. Sci.*, 9 (1979) 43.
- [34] J. Bernard et al., *Surf. Sci.* 3 (1965) 359.
- [35] J. Perdereau and G. E. Rhead, *Surf. Sci.* 7 (1967) 175.
- [36] J. T. Kummer, *J. Phys. Chem.* 60 (1956) 666.
- [37] G. J. Kovacs, *Surf. Sci.* 78 (1978) L245.
- [38] H. E. Bennett et al., *J. App. Phys.* 40 (1969) 3351.

- [39] S. Lilienfeld and C. E. White, *J. Am. Chem. Soc.* 52 (1930) 885.
- [40] E. Peters, *Corrosion Sci.* 6 (1966) 235.
- [41] A. A. Fote, SAMSO-TR-77-91 (The Aerospace Corp., El Segundo Calif., 1977).
- [42] P. A. Kilty and W. M. H. Sachtler, *Cat. Rev.*, 10 (1974) 1.
- [43] B. L. Butler (ed.), *Basic and Applied Research Program: Semiannual Report, SERI/TR-334-244* (Solar Energy Research Institute, Golden, CO, Dec. 1979).
- [44] K. Tsuji and T. Seiki, *J. Polym. Sci. B8* (1970) 817.
- [45] K. Tsuji and T. Seiki, *Polym. J.* 2 (1971) 606.
- [46] C. H. Bamford and C. F. H. Tipper (eds.), *Degradation of Polymers* (Elsevier, New York, 1975).
- [47] K. J. Saunders, *Organic Polymer Chemistry* (Chapman and Hall, London, 1977).
- [48] W. L. Hawkins (ed.), *Polymer Stabilization* (Wiley-Interscience, New York, 1972).
- [49] J. C. Siegle, *J. Polym. Sci. A2* (1964) 391.

- [50] S. T. H. Lee, Picatinny Arsenal Tech. Report 2462G1, (1966).
- [51] L. Reich et al., Picatinny Arsenal Tech. Report 0061H4.
- [52] P. P. Luff et al., Vacuum 18 (1968) 437.
- [53] F. B. Yurevich, Vesti, Akad. Nauk. B SSR Ser. Fiz. Energ. Navuk 2 (1976) 65.
- [54] S. Morisaki, Therm. Anal. (Proc. Int. Conf.) 5th (1977) 297.
- [55] S. L. Madorsky et al., J. Res. Nat. Bur. Stds. 51 (1953) 327.
- [56] R. H. Hansen et al., J. Polym. Sci. A3, No. 6 (1965) 2205.
- [57] a. K. L. Paciorek et al., J. Polym. Sci. Chem. Ed. 11 (1973) 1465.
b. R. L. Daubendiek and J. G. Calvert, Environ. Lett. 6 (1974) 253.
- [58] L. A. Wall et al., J. Res. Nat. Bur. Stds. 65A (1961) 227.
- [59] R. E. Florin et al., J. Res. Nat. Bur. Stds. 65A (1961) 375.
- [60] W. B. Ard, H. Shields, and W. Gordy, J. Chem. Phys. 23 (1955) 1727.
- [61] S. L. Madorsky et al., J. Res. Nat. Bur. Stds. 55 (1955) 223.
- [62] V. F. Shevchenko, Nauch, Tr. Tashkent. Univ. #403, (1971) 84.

- [63] S. L. Madorsky et al., J. Res. Nat. Bur. Stds. 62 (1959) 219.
- [64] D. A. Rodchenko et al., Tezisy. Dokl.-Resp. Konf Vysokomol. Soedin 3rd.
- [65] B. Ranby and J. F. Rabek, Photodegradation, Photo-Oxidation and Photo-stabilization of Polymers: Principles and Applications (Wiley, New York, 1975).
- [66] Modern Plastics Encyclopedia, Vol. 54, No. 10A (McGraw-Hill, Inc., New York, 1977).
- [67] L. A. Wall et al., J. Polym. Sci. A-1, 4 (1966) 349.
- [68] S. L. Madorsky et al., J. Res. Nat. Bur. Stds. 63A (1959) 261.
- [69] H. Schonhorn et al. (Adhesion Society, Savanna, GA, Feb. 1979).
- [70] H. Arito, Ind. Health 10 (1972) 107.
- [71] Y. Murakami et al., Thin Solid Films 9 (1972) 301.
- [72] G. H. Bowers et al., Ind. Eng. Chem, Prod. Res. Dev. 1 (1962) 89.
- [73] A. F. Forestieri and E. Anagnostou, Real-Time and Accelerated Outdoor Endurance Testing of Solar Cells, ERDA/NASA/1022-77/17, NASA TM-73743 (NASA, Lewis Research Center, Cleveland, OH, Sept. 27, 1977).

- [74] Springborn Laboratories, Investigation of Test Methods, Material Properties, and Processes for Solar Cell Encapsulants, ERDA/JPL-954527-77/2 (Enfield, CT, July 1977).
- [75] J. L. Cotter et al., *J. Polym. Sci., Part B*, 6 (1968) 763.
- [76] N. Grassie, *Chemistry of High Polymer Degradation Processes* (Butterworth, London, 1956).
- [77] S. L. Madorsky, *J. Polym. Sci.* 11 (1953) 491.
- [78] A. Jamieson and I. C. McNeill, *J. Polymer Sci. Polymer Chem. Ed.* 16 (1978) 2225.
- [79] I. C. McNeill, *Eur. Polym. J.* 4 (1968) 21.
- [80] I. C. McNeill and D. Neil, *Eur. Polym. J.* 6 (1970) 143.
- [81] I. C. McNeill and D. Neil, *Eur. Polym. J.* 6 (1970) 569.
- [82] A. Jamieson and I. C. McNeill, *J. Polym. Sci. Polym. Chem. Ed.* 14 (1976) 1839.
- [83] H. H. Jellinek, *J. Phys. Chem.* 70 (1966) 3672.
- [84] A. Gupta, *Low-Cost Solar Array*, (Jet Propulsion Laboratory, Pasadena, CA, Aug. 10, 1978).

- [85] L. G. Rainhart and W. P. Schimmel, Jr., *Solar Energy* 17 (1975) 259.
- [86] K. Morimoto et al., *J. App. Polym. Sci.* 16 (1972) 294.
- [87] R. B. Fox et al., *U. S. Naval Res. Lab. Report #5720* (1961).
- [88] R. B. Fox et al., *J. Polym. Sci. A1* 1 (1963) 1079.
- [89] J. P. Allison, *J. Polym. Sci. A1* 4 (1966) 1209.
- [90] L. Ackerman et al., *J. S. African Chem. Inst.* 27 (1974) 105.
- [91] R. E. Michel et al., *J. Chem. Phys.* 45 (1966) 4604.
- [92] A. R. Shultz, *J. Phys. Chem.* 65 (1961) 967.
- [93] T. R. Price et al., *U. S. Naval Res. Lab. Report #6563* (Washington, DC, 1967).
- [94] H. Schonhorn et al., *J. Phys. Chem.* 70 (1966) 3811.
- [95] B. Rosen, *J. Polym. Sci.* 47 (1960) 19.
- [96] B. Rosen, *J. Polym. Sci.* 49 (1961) 177.
- [97] R. E. Barker, *J. Polym. Sci.* 58 (1962) 553.

- [98] F. Bueche, J. Polym. Sci. 14 (1954) 414.
- [99] Modern Plastics Encyclopedia (McGraw-Hill, Inc., New York, 1977-1978) p. 495.
- [100] D. T. Clark et al., J. Polym. Sci. 14 (1976) 1701.
- [101] J. B. Heaney, Evaluation of Commercially Supplied Silver Coated Teflon for Spacecraft Temperature Control Usage, NASA-TM-X-70588 (Goddard Space Flight Center, Greensley, MD, Jan. 1974).
- [102] M. C. St. Cyr, NTIS AD261549 (1961).
- [103] A. F. Forestieri et al., Interscience Energy Conversion Engineering Conf. Proceedings (1971) p. 881.
- [104] A. A. Benderly, J. Appl. Polym. Sci. 6 (1962) 221.
- [105] D. M. Mattox, J. Appl. Phys. 34 (1963) 2493.
- [106] H. Schonhorn et al., J. Appl. Polym. Sci. 11 (1967) 1461.
- [107] H. Schonhorn et al., J. Adhesion 2 (1970) 93.
- [108] G. M. Sessler et al., J. Appl. Polym. Sci. 17 (1973) 3199.
- [109] K. Bhasin et al., Thin Solid Films 45 (1977) 195.

- [110] R. K. Traeger, IEEE Trans. on Parts, Hybrids and Packaging, Vol. PHP-13, No. 2 (June 1977).
- [111] E. I. duPont de Nemours and Co. (Inc.), Bulletin E-21605 (August 1978).
- [112] F. G. Cunningham et al., Nat. Bur. Stds., Spec. Pub. #336 (1970) p. 345.
- [113] H. J. Moore, Jr., and J. H. Donnelly, Jr., Evaluation of High-Temperature Stranded Hook-Up Wire, NASA TM-X-53522 (June 1966).
- [114] J. Fock, J. Polym. Sci. Polym. Lett. Ed. 6 (1968) 127.
- [115] K. A. Klinedinst et al., J. Mater. Sci. 11 (1976) 209.
- [116] a. P. Lindenmeyer, Inter. Conf. on Mechanical Behavior of Materials, Kyoto, Japan (Aug. 15, 1971).
- b. P. Lindenmeyer, Principles of Nonlinear Irreversible Thermodynamics Applied to the Testing of Materials, Boeing Document D180-25583-1 (Boeing Co., Seattle, WA, Jan. 1980).
- [117] R. H. Hansen, in: Thermal Stability of Polymers, ed. R. T. Conley (Dekker, New York, 1970) p. 153.

Table 1. Commercial Fluorocarbon Polymers^a

Generic Name	Abbreviation	Structural Repeat Unit	Trade Name	Manufacturer
Polytetrafluoroethylene	TFE	$\begin{array}{c} \text{F F} \\ \\ -\text{C}-\text{C}- \\ \\ \text{F F} \end{array}$	Teflon	Du Pont
Polychlorotrifluoroethylene	CTFE	$\begin{array}{c} \text{Cl F} \\ \\ -\text{C}-\text{C}- \\ \\ \text{F F} \end{array}$	Aclar Kel F	Allied 3M
Polyvinyl fluoride	VF	$\begin{array}{c} \text{H H} \\ \\ -\text{C}-\text{C}- \\ \\ \text{H F} \end{array}$	Tedlar	Du Pont
Polyvinylidene fluoride	VDF	$\begin{array}{c} \text{H F} \\ \\ -\text{C}=\text{C}- \\ \\ \text{H F} \end{array}$	Kynar	Pennwalt
Tetrafluoroethylene-hexafluoropropylene copolymer	FEP	$\left[\begin{array}{c} \text{F F} \\ \\ -\text{C}-\text{C}- \\ \\ \text{F F} \end{array} \right]_{5-25} \left[\begin{array}{c} \text{F CF}_3 \\ \\ -\text{C}-\text{C}- \\ \\ \text{F F} \end{array} \right]$	"Teflon" FEP	Du Pont
Perfluoroalkoxy-substituted polytetrafluoroethylene	PFA	$\left[\begin{array}{c} \text{F F} \\ \\ -\text{C}-\text{C}- \\ \\ \text{F F} \end{array} \right] \left[\begin{array}{c} \text{F F} \\ \\ -\text{C}-\text{C}- \\ \\ \text{FOC}_n\text{F}_{2n+1} \end{array} \right]$	"Teflon" PFA	DuPont
Ethylene-tetrafluoroethylene copolymer	E-TFE	$\begin{array}{c} \text{H H F F} \\ \\ -\text{C}-\text{C}-\text{C}-\text{C}- \\ \\ \text{H H F F} \end{array}$	Tefzel	Du Pont
Ethylene-chlorotrifluoroethylene copolymer	E-CTFE	$\begin{array}{c} \text{H H Cl F} \\ \\ -\text{C}-\text{C}-\text{C}-\text{C}- \\ \\ \text{H H F F} \end{array}$	Halar	Allied

^a Reference 11.

**Table 2. REACTIVITY OF SEVERAL
POLYMERS WITH OXYGEN
ATOMS**

Material	Rate of Reaction (g x 10⁴/cm²/min)
TFE	0.13
FEP	0.09
VF	0.52
PMMA	0.44

Table 3. THERMAL STABILITY OF POLYMERS

Polymer	Temperature for 50% Weight Loss in 30 minutes (°C)
Teflon TFE	510
Teflon FEP	ca. 510
Polyvinylidene fluoride	445 ^a
Poly-p-xylylene	435
Polymethylene	415
Polyvinylfluoride	388
Kel-F	380
Polystyrene	365
PMMA	325

^aForms char.