# Film Lamination by Radiation-Induced Polymerization of Acrylic Acid

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## Synopsis

Monomeric acrylic acid when placed between two polymeric films may be polymerized almost explosively at a dose of 0.3 Mrad with electrons.   The resultant exotherm leads to bonding of the two films and the preparation of an interlaminar layer of polyacrylic acid. Changes in oxygen permeability are found for the resultant sandwich.   The exotherm and the resultant bonding is dependent on the dose rate, dose, and the volume of acrylic acid used for the interlaminar layer.   The results qualitatively follow the mechanism for explosive polymerization discussed by Semenov and more recently by Chachaty, Magat, and Ter Minassian.

## INTRODUCTION

The lamination of films to give two-, three-, and four-ply composites have been reported in the literature,[1] and these films are now being commercially produced.   Generally these composites are formed by using techniques such as heat plus pressure, adhesives, electric discharges, flaming, and further polymerization or crosslinking of prepolymers.   We have now used the phenomenon of radiation-induced explosive polymerization of acrylic acid[2] to form not only a bond between two polymeric films but also a discrete poly(acrylic acid) layer.   The resultant material is a three-ply composite.   Up to this time, the preparation of a continuous poly(acrylic acid) film has proven difficult because of the brittleness of the polymer.

## EXPERIMENTAL

### Irradiation Equipment and Procedure

All irradiations were accomplished with 2 M.e.v. electrons by using a 2 M.e.v. Van de Graaff electron accelerator.   Dosimetry was determined both by the blue cellophane technique of Henley[3] and the oxalic acid method of Dragonic.[4]   With our accelerator, a dose of 1.3 Mrad is achieved in thin films in a single pass by using a pass rate of 18.4 in./min., a scan width of 12 in. and a beam current of 195 $\mu$amp.   For a smaller dose per pass, the beam current was adjusted accordingly.   The conveyor belt was so arranged that the interval between successive passes under the beam could be varied from

three minutes to twenty minutes. All irradiations were conducted in air with the sample on a styrofoam insert placed in an aluminum tray. No effort was made to control the temperature of the sample before, during, or after the irradiation unless specifically stated.

## Description of Monomers and Polymers

All polymer films were commercially available materials. These films were used as received with no prior treatment to remove surface contamination. The polymers used were the following: (1) Grex, 0.96 density ethylene, 1 mil thick, (Polymer Chemical Division, W. R. Grace); (2) polypropylene, film grade, 1 mil thick (Hercules Co.); (3) low-density polyethylene film, 1 mil thick, (duPont Co.); (4) type L irradiated low-density polyethylene film, 1 mil thick (Cryovac Division, W. R. Grace); (5) type D irradiated film, mixture of low- and high-density polyethylenes, 1 mil thick (Cryovac Division of W. R. Grace); (6) Mylar, poly(ethylene terephthalate), 8 mils thick (Gilbert Plastics); (7) Teflon film, polytetrafluoroethylene, 2 mils (Gilbert Plastics); (8) poly(vinyl chloride), plasticized but unstabilized, 5 mils (Dewey and Almy Division, W. R. Grace); (9) Saran, presumably poly(vinylidene chloride), 1 mil (Dow Corp.); (10) aluminum foil, 1 mil (Reynolds Aluminum Co.); (11) polystyrene, biaxially oriented, 1 mil (Cryovac Division, W. R. Grace); (12) nylon 66, 75 mils (Gilbert Plastics); (13) poly(methyl methacrylate), 25 mils (Gilbert Plastics).

Acrylic acid was obtained from Eastman Kodak Co., Catalog No. 3588, and was used without purification. The other acrylic monomers used in our investigation, namely, 2-ethylhexyl acrylate, stearyl methacrylate, butyl methacrylate, $\beta$-hydroxyethyl methacrylate, 1,3-butylene dimethacrylate, lauryl methacrylate, and ethyl acrylate were obtained from Rohm and Haas and were used without further purification. Acrylonitrile was supplied by Fisher Scientific Company, the 2-vinylpyridine by Reilly Tar and Chemical Co. and the N-vinyl-2-pyrrolidone by General Aniline and Film.

## Lamination of Films (Sandwich)

Films were laminated by the following procedure using acrylic acid. Both polymer film A and polymer film B were cut into 4 in. by 4 in. strips. Between the two strips, there was placed 2–32 drops of the monomer or comonomer composition (each drop weighed approximately 0.019 g.). The composite was then irradiated at the described dose with the final adhesion being estimated qualitatively or measured by a lap adhesion shear test (similar to ASTM-D-1002-64). Oxygen permeability was determined by a Zwick volumetric type (Z-170) apparatus supplied by Zwick and Co. The percentage thickness of the polyacrylic or copolymer interlaminar film was determined by measurement of the thickness of the original films making up the laminate and then that of the laminate. The difference in thickness was assumed to be the thickness of the interlaminar layer.

## RESULTS

Acrylic acid was the monomer of choice after it was shown that 22 of the more common monomers gave neither the desired discrete polymeric layer nor bonding at radiation doses up to 5.0 Mrad. Then for acrylic acid, the conditions of irradiation and concentration for forming a discrete poly-(acrylic acid) layer and for accomplishing bonding were determined.

Selecting a coverage of 0.033 g. of acrylic acid per square centimeter of polymer film, we determined the qualitative dependence of bonding on both dose and dose per pass for 1 mil thick high-density polyethylene. The results are given in Table I. For the acrylic acid coverage used for bonding, a minimum dose per pass of about 0.1 Mrad and a minimum dose of approximately 0.3 Mrad was required. However, the experiments showed that better bonding was found if the total dose of 0.3 Mrad was delivered in a single pass.

The effect of variation in the amount of acrylic acid used per unit area on the effectiveness of bonding was determined. The results are given in Table II.

TABLE I
Effect of Dose and Dose Per Pass on Acrylic Acid Bonding[a]

| Dose, Mrad | Dose per pass, Mrad | Bonding (qualitative)[b] |
|---|---|---|
| 0.1 | 0.1 | 0 |
| 0.2 | 0.1 | 0 |
| 0.2 | 0.2 | 0.5 |
| 0.3 | 0.1 | 0 |
| 0.3 | 0.3 | 3 |
| 0.4 | 0.1 | 1 |
| 0.4 | 0.2 | 2 |
| 0.4 | 0.4 | 3 |
| 0.5 | 0.1 | 1 |
| 0.5 | 0.5 | 4 |
| 0.7 | 0.1 | 1.5 |

[a] Pass time, 3 min.; exposure time to electron beam per pass, 12 sec.

[b] To describe the bonding, numbers were assigned. No bonding was represented as 0, poor bonding 1; fair bonding, 2; good bonding, 3; excellent bonding, 4. To describe bonding that was intermediate between two classes, 0.5 was added to the lower number.

TABLE II
Effect of Acrylic Acid Coverage on Excellence of Bonding

| Acrylic acid coverage, g./cm.$^2$ | Bonding (qualitative)[a] |
|---|---|
| 0.028 | 4 |
| 0.009 | 4 |
| 0.003 | 4 |
| 0.001 | 3.5 |
| 0.0003 | 1 |

[a] The numerical designations are the same as given in Table I.

## TABLE III
### Acrylic Acid as Bonding Agent for Radiation-Induced Lamination[a]

| Material[b] | PP | 0.92 Density PE | Type D | Type L | Mylar | Teflon | PVC | PVCl₂ | Al foil | Oriented PS | Nylon | PMMA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.96 PE | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 1 | 4 |
| PP | | 4 | 4 | 4 | 3 | 4 | 4 | 4 | 4 | 4 | 2 | 3.5 |
| 0.92 PE | | | 4 | 4 | 2.5 | 4 | 4 | 4 | 4 | 4 | 2 | 4 |
| Type D | | | | 4 | 3 | 4 | 2.5 | 4 | 3.5 | 4 | 1 | 1 |
| Type L | | | | | 1 | 2 | 2.5 | 4 | 4 | 4 | 1 | 2.5 |
| Mylar | | | | | | 3 | 1 | 4 | 1.5 | 4 | 1 | 1 |
| Teflon | | | | | | | 2.5 | 3 | 2.5 | 4 | 3 | 3 |
| PVC | | | | | | | | 4 | 1 | 4 | 3 | 3.5 |
| PVCl₂ | | | | | | | | | 4 | 4 | 4 | 4 |
| Al foil | | | | | | | | | | 4 | 1 | 1 |
| Oriented PS | | | | | | | | | | | 2.5 | 4 |
| Nylon | | | | | | | | | | | | 3.5 |

[a] Ratings: 4 = excellent bonding with one of polymer films failing; 3 = good, one of polymer films failed and traces of delamination; 2 = fair, both film failure and delamination; 1 = poor, delaminated easily; 0 = no bonding.

[b] PE is polyethylene; PP is polypropylene; Type D is an oriented polyethylene film marketed by Cryovac; Type L is an oriented polyethylene film marketed by Cryovac; PVC is poly(vinyl chloride), PVCl₂ is poly(vinylidene chloride), Al is aluminum, PS is polystyrene, and PMMA is poly(methyl methacrylate).

TABLE IV
Shear Lap Adhesion Tests on Poly(acrylic Acid)-Bonded Samples

| Materials | | | | Physical testing | |
|---|---|---|---|---|---|
| | Thick- | | Thick- | | |
| | ness A, | | ness B, | Failure, | Failure |
| A | mils | B | mils | psi | location |
| Polypropylene | 10 | Poly(methyl meth-acrylate) | 25 | 64 ± 8 | Film |
| Poly(vinyl chloride) | 5 | Tin plate | 9 | 26.4 ± 1.3 | Film |
| Teflon (0.5 Mrad dose) | 2 | Nylon | 75 | 3.4 ± 0.1 | Film |
| Teflon (0.5 Mrad dose) | 2 | Poly(methyl meth-acrylate) | 25 | 2.5 | Film |
| Polypropylene | 10 | Aluminum plate | 5 | 76 ± 3 | Film |
| Polypropylene | 10 | Tin plate | 9 | 87 ± 7 | Film |
| Polypropylene | 10 | Poly(vinyl chloride) | 5 | 27.3 ± 1.2 | Film |
| Teflon | 2 | Polypropylene | 10 | 1.1 ± 0.2 | Film |
| 0.96 Polyethylene | 10 | Mylar | 8 | 29, 46 | |
| 0.96 Polyethylene | 10 | Tin plate | 9 | 76 | Film |
| 0.96 Polyethylene | 10 | Poly(methyl meth-acrylate | 25 | 96, 71 | Film |
| 0.96 Polyethylene | 10 | 0.96 Polyethylene | 10 | 231 ± 3 | Film |
| 0.96 Polyethylene | 10 | Aluminum foil | 6 | 100 ± 10 | Film |
| 0.96 Polyethylene | 10 | Poly(vinyl chloride) | 5 | 25.8 ± 0.8 | Film |
| 0.96 Polyethylene | 10 | Teflon | 2 | 4.8 ± 0.3 | Film |
| 0.96 Polyethylene | 10 | Polypropylene | 10 | 90 ± 5 | Film |
| 0.96 Polyethylene | 10 | 0.92 Polyethylene | 10 | 15.6 | Film |
| Polypropylene | 15 | Plywood | 250 | 182, 273 | Bond |
| Mylar | 6 | Plywood | 250 | 29.8, 4.4 | Bond |
| Tin plate | 9 | Plywood | 250 | 156, 197 | Bond |

To insure that the dose and dose per pass effect would not enter into the study, the higher dose of 2.0 Mrad at 1.0 Mrad per pass was used.

In an effort to correlate the bonding excellence with the maximum temperature achieved during the polymerization, efforts were made to measure the peak temperature with No. 40 thermocouple wire. Difficulties were encountered in replication of peak temperature measurements under what appeared to be identical experimental conditions. The major difficulty appeared to be the inability to position properly the temperature sensing device to record the peak of the exotherm. However, we were able to measure temperatures as high as 210°C. between polymer films using a single pass at a dose of 1.0 Mrad per pass. Using a dose per pass of 1.0 Mrad and consecutive passes, we found that an exotherm occurred only during the first pass. Using a dose per pass of 0.5 Mrad, we found a reduced exotherm during the first pass. These findings are in accord with the explanation given in the discussion.

Two additional variables were then examined for the acrylic acid, radiation-induced, bonding system: (1) the spectra of materials that could be bonded together by acrylic acid and (2) the effect of comonomer addition on

## TABLE V
### Comonomer Systems for Bonding Polyethylene to Polypropylene[a]

| Acrylic acid, % | Monomer B | Monomer B, % | Lamination | Transparency of bond | Nature of bond | Monomer odor |
|---|---|---|---|---|---|---|
| 90 | N-Vinyl-2-pyrrolidone | 10 | 3 | Good | Tacky | None |
| 80 | | 20 | 3 | Good | Brittle | Acrylic |
| 60 | | 40 | 2 | Opaque | Tacky, brittle | None |
| 40 | | 60 | 2 | Opaque | Brittle | B |
| 20 | | 80 | 2 | Poor | Brittle | B |
| 90 | Methyl methacrylate | 10 | 4 | Good | Flexible | None |
| 80 | | 20 | 4 | Good | Slightly brittle | None |
| 60 | | 40 | 4 | Good | Gummy | B |
| 40 | | 60 | 2 | Good | Tacky | B |
| 20 | | 80 | 1 | Opaque | Tacky | B |
| 90 | Ethyl acrylate | 10 | 4 | Excellent | Flexible | None |
| 80 | | 20 | 4 | Excellent | Flexible | None |
| 60 | | 40 | 4 | Excellent | Flexible | None |
| 40 | | 60 | 4 | Excellent | Flexible | None |
| 20 | | 80 | 4 | Excellent | Flexible | None |
| 90 | Ethyl methacrylate | 10 | 4 | Good | Flexible | None |
| 80 | | 20 | 4 | Good | Flexible | None |
| 60 | | 40 | 4 | Good | Flexible | None |
| 40 | | 60 | 3 | Good | Tacky | B |
| 90 | 2-Vinylpyridine | 10 | 0 | | | |
| 20 | | 80 | 0 | | | |
| 40 | | 60 | 0 | | | |
| 60 | | 40 | 0 | | | |
| 80 | | 20 | 0 | | | |
| 90 | Acrylonitrile | 10 | 3 | Good | Brittle | None |
| 80 | | 20 | 3 | Good | Brittle | None |

| | | Monomer | | | | |
|---|---|---|---|---|---|---|
| 60 | 40 | | 3 | Good | Brittle | None |
| 40 | 60 | | 3 | Good | Brittle | None |
| 20 | 80 | | 3 | Good | Brittle | None |
| 90 | 10 | Hydroxyethyl methacrylate | 4 | Opaque | Brittle | None |
| 80 | 20 | | 4 | Opaque | Brittle | None |
| 60 | 40 | | 4 | Opaque | Brittle | None |
| 40 | 60 | | 4 | Opaque | Brittle | None |
| 20 | 80 | | 2 | Opaque | Brittle | None |
| 90 | 10 | Stearyl methacrylate | 2 | Opaque | Brittle | None |
| 80 | 20 | | 4 | Opaque | Brittle | None |
| 60 | 40 | | 4 | Opaque | Brittle | None |
| 40 | 60 | | 4 | Opaque | Brittle | None |
| 20 | 80 | | 4 | Opaque | Brittle | None |
| 90 | 10 | Lauryl methacrylate | 1 | Fair | Gummy | B |
| 80 | 20 | | 1 | Fair | Very gummy | B |
| 60 | 40 | | 4 | Fair | Brittle | B |
| 40 | 60 | | 4 | Fair | Brittle | B |
| 20 | 80 | | 4 | Fair | Sl. brittle | B |
| 90 | 10 | 1,3-Butylene dimethacrylate | 2 | Good | Brittle | B |
| 80 | 20 | | 2 | Good | Brittle | B |
| 60 | 40 | | 2 | Good | Brittle | B |
| 40 | 60 | | 2 | Good | Brittle | B |
| 20 | 80 | | 2 | Good | Brittle | None |
| 90 | 10 | 2-Ethylhexyl methacrylate | 4 | Good | Flexible | None |
| 80 | 20 | | 4 | Good | Flexible | None |
| 60 | 40 | | 2 | Good | Flexible | None |
| 40 | 60 | | 4 | Good | Flexible | None |
| 20 | 80 | | 4 | Good | Flexible | None |
| 90 | 10 | Butyl methacrylate | 2 | Good | Flexible | None |
| 80 | 20 | | 2.5 | Good | Flexible | None |
| 60 | 40 | | 4 | Good | Flexible | None |
| 40 | 60 | | 4 | Good | Flexible | None |
| 20 | 80 | | 4 | Good | Flexible | None |

the bonding. These two variables were examined both individually and together.

Table III, then, gives a matrix for a series of materials that were bonded with the use of acrylic acid only. For this series, the acrylic acid covering was 0.03 g./cm.[2] and the dose was 2.0 Mrad at a dose per pass of 1.0 Mrad. In Table IV, lap adhesion shear test measurements are given for some of these samples. Teflon, by this measurement, was shown to be badly degraded during the bonding step.

The effect of monomer composition in comonomer systems on the polymerization and bonding is shown in Tables V and VI: in Table V for a series of comonomers at 3.0 Mrad dose, in Table VI at varied doses. The exotherm is usually reduced by the introduction of comonomers into the acrylic acid system. However, based on the excellence of bonding at very low doses, ethyl acrylate did not appear to moderate the acrylic acid polymerization exotherm. However with most of the other monomers, a larger dose is required to achieve the necessary bonding exotherm.

For Tables VII–XI, a number of the comonomer compositions were more exhaustively tested. Only comonomer compositions which gave a bonding exotherm at a dose of 1.0 Mrad were employed. In Table XII, we have demonstrated that the nature of the comonomer composition as well as the exotherm is important in the relative degree of bonding.

Finally in Table XIII, oxygen permeability values are given for some untreated and for some three-ply films made by our bonding procedure. From these values and using the equation presented in the discussion, we were able to calculate approximately the specific oxygen permeability of the interlaminar bonding films.

## DISCUSSION

### Bonding

Acrylic acid explosive polymerizations have been shown to occur in bulk by use of conventional chemical initiation, e.g., azobisisobutyronitrile, irradiation-initiation,[2] and freezing and melting of the monomer.[5] Such explosive polymerizations may be readily explained on the basis of the original Semenov[6] equation which has been amplified by Chachaty, Magat, and Ter Minassian.[7,8] The critical variables in the equation are: the rate of polymerization, the energy of activation for the polymerization, the heat of polymerization, the number of initiating radicals, the volume element for the polymerization and its relation to the surface area, and the specific heat and heat conductivity of the polymerizing medium.

The equation proposed by Semenov is

$$\gamma VC(dT_i/dt) = -kS(T_i - T_e) + VQCC^*A_p \exp\{E_p/RT_i\} \quad (1)$$

where $\gamma$ is the specific heat of the monomer, $V$ is the volume of the reaction medium, $C$ is the concentration of the monomer, $T_i$ is the internal temperature, $k$ is a general rate constant but for our investigation is the rate of

## TABLE VI
### Change in Bonding Excellence with Reduction in Radiation Dose in Bonding of 0.96 Density Polyethylene to Polypropylene

| B, % | Monomer B | Dose, Mrad | Lamina-tion | Transparency of bond | Nature of bond | Monomer odor |
|---|---|---|---|---|---|---|
| 90 | 2-Hydroxyethyl methacrylate | 2.0 | 3 | Good | Flexible | B |
| 80 | | 2.0 | 3 | Good | Flexible | B |
| 60 | | 2.0 | 4 | Good | Less flexible | B |
| 40 | | 2.0 | 4 | Good | Brittle | B |
| 20 | | 2.0 | 4 | Good | Flexible | B |
| 90 | Stearyl methacrylate | 5.0 | 2 | Good | Flexible | B |
| 80 | | 5.0 | 1 | Good | Flexible | B |
| 60 | | 2.0 | 4 | Good | Flexible | B |
| 40 | | 1.0 | 4 | Good | Less flexible | B |
| 20 | | 1.0 | 4 | Good | Brittle | B |
| 40 | Stearyl methacrylate | 0.75 | 4 | Good | Flexible | None |
| 40 | Stearyl methacrylate | 0.5 | 2 | Good | Tacky | None |
| 20 | | 0.5 | 2 | Good | Tacky | B |
| 90 | Lauryl methacrylate | 5.0 | 1 | Good | Sticky | B |
| 80 | | 5.0 | 1 | Good | Sticky | B |
| 60 | | 2.0 | 3 | Good | Flexible | B |
| 40 | | 2.0 | 3 | Good | Flexible | B |
| 20 | | 1.0 | 4 | Good | Flexible | B |
| 90 | 1,3-Butylene dimethacrylate | 1.0 | 1 | Good | Dry | B |
| 80 | | 1.0 | 1 | Good | Dry | B |
| 60 | | 1.0 | 1 | Good | Dry | B |
| 40 | | 1.0 | 4 | Good | Flexible | B |
| 20 | | 1.0 | 4 | Good | Flexible | B |
| 40 | 1,3-Butylene dimethacrylate | 0.75 | 1 | Fair | None | B |
| 20 | | 0.75 | 1 | Fair | None | B |

TABLE VI (continued)

| B, % | Monomer B | Dose, Mrad | Lamination | Transparency of bond | Nature of bond | Monomer odor |
|---|---|---|---|---|---|---|
| 20 | 1,3-Butylene dimethacrylate | 0.5 | 1 | Good | Tacky | B |
| 40 | | 0.5 | 1 | Good | Tacky | B |
| 60 | | 0.5 | 1 | Good | Tacky | B |
| 80 | | 0.5 | 1 | Good | Tacky | B |
| 90 | | 0.5 | 1 | Good | Tacky | B |
| 90 | n-Butyl methacrylate | 5.0 | 0 | | | |
| 80 | | 5.0 | 0 | | | |
| 60 | | 5.0 | 4 | Good | Flexible | B |
| 40 | | 3.0 | 4 | Good | Flexible | B |
| 20 | | 2.0 | 4 | Good | Brittle | B |
| 80 | n-Butyl methacrylate | 1.0 at 0.5 per pass | 3 | Good | Sticky | B |
| 60 | | | 1 | Good | | B |
| 40 | | | 3 | | Sticky | B |
| 60 | n-Butyl methacrylate | 0.75 | 0 | | | |
| 40 | | 0.75 | 0 | | | |
| 20 | | 0.75 | 0 | | | |
| 90 | Ethyl acrylate | 1.0 | 3 | Good | Tacky | Acrylic |
| 80 | | 1.0 | 3 | Good | Tacky | Acrylic |
| 60 | | 1.0 | 4 | Good | Flexible | None |
| 40 | | 1.0 | 4 | Good | Flexible | None |
| 20 | | 1.0 | 4 | Good | Flexible | None |
| 90 | Ethyl acrylate | 0.5 | 4 | | | |
| 80 | | 0.5 | 4 | | | |
| 60 | | 0.5 | 4 | | | |
| 40 | | 0.5 | 4 | | | |
| 20 | | 0.5 | 4 | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| Ethyl acrylate | 90 | 0.4 | 4 | Good | Flexible | None |
| | 80 | 0.4 | 4 | Good | Flexible | None |
| | 60 | 0.4 | 4 | Good | Flexible | None |
| | 40 | 0.4 | 4 | Good | Flexible | None |
| | 20 | 0.4 | 4 | Good | Flexible | None |
| Ethyl acrylate | 90 | 0.25 | 2 | Good | Sticky | B |
| | 80 | 0.25 | 2 | Good | Sticky | B |
| | 60 | 0.25 | 2 | Good | Sticky | B |
| | 40 | 0.25 | 2 | Good | Sticky | B |
| | 20 | 0.25 | 2 | Good | Sticky | B |
| 2-Ethylhexyl methacrylate | 90 | 1.0 | 4 | Good | Flexible | B |
| | 80 | 1.0 | 4 | Good | Flexible | B |
| | 60 | 1.0 | 4 | Good | Flexible | B |
| | 40 | 1.0 | 4 | Good | Flexible | B |
| | 20 | 1.0 | 4 | Good | Flexible | B |
| 2-Ethylhexyl methacrylate | 90 | 0.75 | 4 | Good | Flexible | None |
| | 80 | 0.75 | 4 | Good | Flexible | B |
| | 60 | 0.75 | 3 | Good | Flexible | B |
| | 40 | 0.75 | 2 | Good | Flexible | B |
| | 20 | 0.75 | 2 | Fair | Flexible | B |
| 2-Ethylhexyl methacrylate | 90 | 0.5 | 3 | Good | Sticky | B |
| | 80 | 0.5 | 2 | Good | Tacky | B |
| | 60 | 0.5 | 1 | Good | Not tacky | B |
| | 40 | 0.5 | 1 | Good | Not tacky | B |
| | 20 | 0.5 | 2 | Good | Not tacky | B |

TABLE VII

Bonding with 80% 2-Ethylhexyl Methacrylate[a,b]

| Material | PP | PVC | Mylar | Teflon | Al foil | Tin plate | Saran | 0.92 PE | Plywood | Nylon |
|---|---|---|---|---|---|---|---|---|---|---|
| Grex | 3 | 3 | 3 | 3 | 4 | 3 | 3 | 3 | 1 | 4 |
| PP |  | 4 | 4 | 2 | 4 | 4 | 3 | 4 | 1 | 4 |
| PVC |  |  | 2 | 1 | 4 | 4 | 3 | 4 | 1 | 4 |
| Mylar |  |  |  | 1 | 2 | 1 | 2 | 1 | 1 | 2 |
| Teflon |  |  |  |  | 2 | 3 | 2 | 1 | 1 | 2 |
| Al foil |  |  |  |  |  | 4 | 3 | 3 |  | 3 |
| Tin plate |  |  |  |  |  |  | 4 | 4 | 4 | 4 |
| Saran |  |  |  |  |  |  |  | 4 | 3 | 3 |
| 0.92 PE |  |  |  |  |  |  |  |  | 2 | 4 |
| Plywood |  |  |  |  |  |  |  |  |  | 3 |

[a] Conditions: 1.0 Mrad in one pass, with monomer coverage of 0.01 g./cm.². Residual monomer odor present after all irradiations; [b] Ratings: as in Table III.

TABLE VIII

Bonding with 20% Stearyl Methacrylate[a,b]

| Material | PP | PVC | Mylar | Teflon | Al foil | Tin plate | Saran | 0.92 PE | Nylon | Plywood |
|---|---|---|---|---|---|---|---|---|---|---|
| Grex | 4 | 4 | 1 | 4 | 2 | 3 | 4 | 4 | 4 | 1 |
| PP |  | 4 | 1 | 4 | 3 | 4 | 4 | 4 | 4 | 4 |
| PVC |  |  | 1 | 3 | 2 | 1 | 1 | 4 | 4 | 4 |
| Mylar |  |  |  | 1 | 1 | 1 | 3 | 1 | 1 | 1 |
| Teflon |  |  |  |  | 3 | 4 | 4 | 2 | 4 | 4 |
| Al foil |  |  |  |  |  | 1 | 4 | 2 | 1 | 1 |
| Tin plate |  |  |  |  |  |  | 2 | 1 | 1 | 4 |
| Saran |  |  |  |  |  |  |  | 2 | 2 | 1 |
| 0.92 PE |  |  |  |  |  |  |  |  | 4 | 4 |
| Nylon |  |  |  |  |  |  |  |  |  | 4 |

[a] Conditions: 1.0 Mrad in one pass, with monomer coverage of 0.01 g./cm.². No residual monomer odor; [b] Ratings: as in Table III.

TABLE IX

Bonding with 40% Ethyl Acrylate[a,b]

| Material | PP | PVC | Mylar | Teflon | Al foil | Tin plate | Saran | 0.92 PE | Plywood | Nylon |
|---|---|---|---|---|---|---|---|---|---|---|
| Grex | 4 | 4 | 1 | 4 | 2 | 2 | 4 | 4 | 2 | 4 |
| PP | | 4 | 1 | 4 | 2 | 3 | 1 | 4 | 4 | 4 |
| PVC | | | 1 | 2 | 2 | 2 | 2 | 1 | 1 | 4 |
| Mylar | | | | 2 | 2 | 2 | 1 | 2 | 1 | 1 |
| Teflon | | | | | 2 | 2 | 2 | 4 | 3 | 4 |
| Al foil | | | | | | 2 | 2 | 2 | 2 | 2 |
| Tin plate | | | | | | | 3 | 3 | 3 | 2 |
| Saran | | | | | | | | 2 | 3 | 4 |
| 0.92 PE | | | | | | | | | 1 | 1 |
| Plywood | | | | | | | | | | 4 |

[a] Conditions: 1.0 Mrad in one pass, with monomer coverage of 0.01 g./cm.². Residual monomer odor in most cases; [b] Ratings: as in Table III.

TABLE X

Bonding of Substrates with 60% Ethyl Acrylate[a,b]

| Material | PP | PVC | Mylar | Teflon | Al foil | Saran | 0.92 PE | Plywood | Nylon | Tin plate |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.96 PE | 4 | 4 | 1 | 4 | 2 | 1 | 4 | 1 | 4 | 4 |
| PP | | 4 | 1 | 3 | 3 | 3 | 4 | 0 | 4 | 3 |
| PVC | | | 1 | 2 | 1 | 1 | 4 | 0 | 2 | 1 |
| Mylar | | | | 1 | 1 | 1 | 1 | 0 | 2 | 1 |
| Teflon | | | | | 3 | 3 | 3 | 2 | 3 | 2 |
| Al foil | | | | | | 2 | 1 | 2 | 3 | 2 |
| Saran | | | | | | | 1 | 2 | 2 | 2 |
| 0.92 PE | | | | | | | | 2 | 2 | 2 |
| Plywood | | | | | | | | | 2 | 0 |
| Nylon | | | | | | | | | | 1 |

[a] Conditions: 1.0 Mrad in one pass, with monomer coverage of 0.01 g./cm.². Residual monomer odor in most cases; [b] Ratings: as in Table III.

TABLE XI
Adhesion of Polymer Composites with 80% Ethyl Acrylate[a,b]

| Material | PP | PVC | Mylar | Teflon | Al foil | Saran | 0.92 PE | Plywood | Nylon |
|---|---|---|---|---|---|---|---|---|---|
| 0.96 PE | 3 | 1 | 2 | 3 | 4 | 3 | 4 | 0 | 3 |
| PP | | 1 | 2 | 4 | 3 | 2 | 4 | 0 | 3 |
| PVC | | | 1 | 2 | 1 | 2 | 1 | 0 | 1 |
| Mylar | | | | 2 | '2 | 1 | 1 | 0 | 2 |
| Teflon | | | | | 2 | 3 | 4 | 0 | 4 |
| Al foil | | | | | | 3 | 1 | 0 | 1 |
| Saran | | | | | | | 2 | 0 | 2 |
| 0.92 PE | | | | | | | | 0 | 3 |
| Plywood | | | | | | | | | 1 |

[a] Conditions: 1.0 Mrad in one pass, with monomer coverage of 0.01 g./cm.². All samples had a residual odor of ethyl acrylate.

[b] Ratings: as in Table III.

polymerization, $S$ is the surface area of the reaction medium, $T_e$ is the external temperature, $Q$ is the heat of polymerization, $C^*$ is the concentration of growing chains, $A_p$ is the Arrhenius constant, and $E_p$ is the activation energy for polymerization.

The critical conditions for explosion as described by Chachaty et al.[7,8] are:

$$\varphi = (VQA/kS)CC^*(E_p/RT_e^2) \exp \left\{ E_p/RT_i \right\} \geqq 1/e$$

where $e = 2.718$.

We have then attained the critical value for explosion, namely $\varphi \geqq 1/e$, by a number of methods. First, we have been able to increase the volume-to surface area ratio, the $VQA/kS$ term in the Semenov equation, by maintaining the same surface area but adding more acrylic acid. This has produced the explosive bonding. We also have been able to increase the term $C$ in the equation by adding more acrylic acid. The term $C^*$ or the number of growing chains has been increased by increasing the dose. The result of this increase has been shown in the experimental section, where an increase in the original dose per pass has led to a greater exotherm and improved bonding.

All of the remainder of the terms in the equation are specific for acrylic acid and are substantially unchanged for any variation in dose or in concentration of acrylic acid. These terms are $\gamma$, $k$, $Q$, $A_p$, and $E_p$. To explain the differences in the bonding and exotherm between the various monomeric systems, one or more of these terms should be substantially changed in comparison to those for other monomers or for comonomers. McCurdy and Laidler,[9] however, have shown that the heat of polymerization, $Q$ at 25°C. for both acrylic acid and acrylic esters ranges from 18.4 to 19.0 kcal./mole. Thus, differences in $Q$ do not account for both the explosive polymerization of acrylic acid and the absence of such polymerization for the acrylate esters. In addition, for the methacrylates, the same authors, as

TABLE XII

Comparison of Bonding with Different Comonomer Systems

| Comonomer composition[a] | 0.96 PE | PP | 0.92 PE | Mylar | PVC | Saran | Al foil | Nylon | PMMA | Plywood | Kel-F |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Teflon to** | | | | | | | | | | | |
| Acrylic, 100 | 4 | 4 | 4 | 3 | 2 | 3 | 2 | 3 | 3 | 4 | 1 |
| Stearyl, 20 | 4 | 4 | 2 | 1 | 3 | 4 | 3 | 4 | 2 | 3 | 2 |
| Ethyl, 40 | 4 | 4 | 4 | 2 | 2 | 2 | 2 | 4 | 2 | 2 | |
| Ethyl, 60 | 4 | 4 | 3 | 1 | 2 | 3 | 3 | 3 | | 0 | |
| Ethyl, 80 | 3 | 4 | 4 | 2 | 2 | 3 | 2 | 4 | | 1 | |
| Octyl, 80 | 3 | 2 | | 1 | 1 | 2 | 2 | 2 | 2 | | 2 |
| **Aluminum to** | | | | | | | | | | | |
| Acrylic, 100 | 4 | 4 | 4 | 1 | 1 | 4 | | 1 | 4 | 1 | 1 |
| Stearyl, 20 | 2 | 3 | 2 | 1 | 2 | 4 | | 1 | 3 | 2 | 2 |
| Ethyl, 40 | 2 | 2 | 2 | 2 | 2 | 2 | | 2 | 1 | 2 | |
| Ethyl, 60 | 2 | 2 | 1 | 1 | 1 | 2 | | 3 | | 0 | |
| Ethyl, 80 | 2 | 3 | 1 | 2 | 1 | 3 | | 1 | | 2 | |
| Octyl, 80 | 4 | 4 | | 2 | 4 | 3 | | 3 | 1 | | 2 |
| **Mylar to** | | | | | | | | | | | |
| Acrylic, 100 | 4 | 3 | 2 | | 1 | 4 | | 1 | 1 | 1 | 1 |
| Stearyl, 20 | 1 | 1 | 1 | | 1 | 3 | | 1 | 1 | 1 | 1 |
| Ethyl, 40 | 1 | 1 | 2 | | 1 | 1 | | 1 | 4 | 0 | |
| Ethyl, 60 | 1 | 1 | 1 | | 1 | 1 | | 2 | | 0 | |
| Ethyl, 80 | 2 | 2 | 1 | | 1 | | | 2 | | 1 | |
| Octyl, 80 | 3 | 4 | 1 | | 2 | | | 2 | 1 | | 1 |

[a] Octyl is 2-ethylhexyl methacrylate, stearyl is stearyl methacrylate, ethyl is ethyl acrylate, and acrylic is acrylic acid. The number following these designations represents the percentage of the monomer in the comonomer mixture.

TABLE XIII
Oxygen Permeability of Sandwich Films

| Sample no. | Polymer | Polymer thickness, mils | Monomer composition | % of sandwich | Specific oxygen permeability $\times 10^{-3}$, cc.-mil/atm.-m.$^2$-day[b] | |
|---|---|---|---|---|---|---|
| | | | | | Composite | Polymerized layer |
| 1 | 0.96 PE | 1 | Acrylic acid | 14 | 0.495 | 0.070 |
| 2 | | | | 10 | 0.639 | 0.067 |
| 3 | | | | 7.7 | 0.532 | 0.043 |
| 4 | | | | 4.9 | 0.803 | 0.043 |
| 5 | | | None | | 9.36 | Avg. 0.055 |
| 6 | PP | 1 | Acrylic acid | 16 | 0.650 | 0.116 |
| 7 | | | | 16 | 0.648 | 0.116 |
| 8 | | | | 17 | 0.644 | 0.123 |
| 9 | | | None | | 4.400 | Avg. 0.119 |
| 10 | 0.96 PE | 1 | 20% Stearyl M-80A | 26 | 0.623 | 0.170 |
| 11 | | | 40% Ethyl M-60% A | 26 | 2.400 | 0.772 |
| 12 | | | 60% Ethyl M-40% A | 23 | 2.224 | 0.616 |
| 13 | | | 80% Ethyl M-20% A | 21 | 0.865 | 0.192 |
| 14 | | | 80% 2-Ethyl A-20%c | 19 | 1.455 | 0.328 |
| 15 | | | None | | 9.36 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 16 | PP | 1 | 20% Stearyl M–30% A | 18 | 1.317 | 0.339 |
| 17 | | | 40% Ethyl M–40% A | 13 | 2.155 | 0.498 |
| 18 | | | 60% Ethyl M–40% A | 22 | 2.610 | 1.078 |
| 19 | | | 80% Ethyl-M–20% A | 26 | 4.64 | 5.48 |
| 20 | | | 80% 2-Ethyl A–20% A | 17 | 4.01 | 2.78 |
| 21 | | | None | | 4.40 | |
| 22 | Type L | 1 | None | | 8.87 | |
| 23 | | | Acrylic acid | 18 | 4.98 | 1.63 |
| 24 | Oriented PS | 1 | None | | 1.958 | |
| 25 | | | Acrylic acid | 15 | 1.603 | 0.80 |
| 26 | Type D | 1 | None | | 9.48 | |
| 27 | | | Acrylic acid | 16 | 1.85 | 0.354 |
| 28 | Plasticized PVC | 5 | None | | 0.633 | |
| 29 | | | Acrylic acid | 5.9 | 0.458 | 0.085 |
| 30 | 0.92 PE | 4 | None | | 7.92 | |
| 31 | | | Acrylic acid | 4.4 | 2.41 | 0.150 |

[a] The monomer composition is abbreviated when a comonomer is used with acrylic acid; stearyl M is stearyl methacrylate, ethyl M is ethyl methacrylate, 2-ethyl A is 2-ethylhexyl acrylate, and A is acrylic acid.

[b] The value is for cubic centimeters of oxygen passing through one square meter of one mil thick film at a pressure of 1 atmosphere in one day.

well as Dainton et al.,[10] have found heats of polymerization in the range of 12–14 kcal./mole. Despite this difference between acrylates and methacrylates, 2-ethylhexyl methacrylate has been found at high comonomer fractions to polymerize and bond satisfactorily, while a number of the acrylate esters did not. Examining the other terms, we would anticipate in the liquid phase very little difference in $\gamma$ and $A_p$ for this series of monomers. In the absence of physical measurements, gross differences in either $k$ or in $E_p$ or in both should account for major differences in the dose required for explosive polymerization with subsequent bonding.

However bonding, as would be expected, is not entirely a function of the exotherm developed during the polymerization. This can be shown by the difference in bonding excellence of various materials using acrylic acid and a comonomer compositions. For example, in Table XII, polypropylene bonding to Teflon is far superior with acrylic acid than with 80% 2-ethylhexyl methacrylate–20% acrylic acid. However the reverse order is found for poly(vinyl chloride) to aluminum.

## Permeability

The permeability modifications were measured by determining the specific oxygen permeabilities of the laminates. This method permitted the determination not only of the total permeability of the laminate but also, by an approximate equation, the permeability of the interlaminar polyacrylic or copolymer layer. Previous experimental studies on permeability of laminates were conducted by Morgan.[11] Discussion of the theory of permeability in laminated films is given by Stannett et al.[12a]

The equation that we used for determining the specific oxygen permeability of the interlaminar film was analogous to that for determining electrical conductances in series and is similar to that of Stannett et al. The assumptions inherent in this equation are as follows.

(1) The two films forming the exterior of the sandwich have not been modified during the formation of the polyacrylic acid interlaminar layer. (This was not strictly true, since homopolymer or possible grafting was detected in the exterior films by infrared absorption measurements.)

(2) Conductivity and permeability have been equated in their effect. However, conductivity in electricity is regarded as a function of electron transport while oxygen permeability is based not only on transport but on solubility. This difference may be relatively unimportant, as indicated by a recent paper by Frisch.[13]

(3) The volume of oxygen diffusing through the membrane is inversely proportional to the membrane thickness. Although widely used, this assumption is of doubtful validity.

The final equation, normalized to 1 for the thickness of the sandwich, is then

$$1/P_{ABC} = x/P_A + y/P_B + z/P_C$$

where $P_{ABC}$ is the permeability of the sandwich, $P_A$ is the permeability of one of the exterior films and $x$ is the thickness fraction of this film, $P_C$ is the permeability of the other exterior film and $z$ is the thickness fraction of this film, and $P_B$ is the permeability of the poly(acrylic acid) layer and $y$ is the thickness fraction. When the two exterior films are the same, the equation reduces to

$$1/P_{ABC} = (x + z)/P_A + y/P_B$$

This equation is then the same form as that derived by Stannett,[12a] with the difference that our equation has been normalized to unity because of the use of specific permeability values. Since for our systems, we know the permeability of the exterior films and the permeability of the sandwiches, an approximate value for the oxygen permeability of the polyacrylic acid or copolymer layer could be readily calculated. Previous measurements of oxygen permeability have shown that with increasing electronegative groups present in the polymer, the oxygen permeability is generally reduced.[12b] In accord with this, the oxygen permeability of poly(acrylic acid) is shown to be less than that of polyethylene and of polypropylene. On the other hand, copolymerization with other monomers decreased the polymer regularity and appeared to increase the oxygen permeability.

## References

1. *Mod. Plastics*, **42**, No. 6, 47 (1965).
2. Marans, N., unpublished results.
3. Henley, E. J., and D. Richman, *Anal. Chem.*, **28**, 1580 (1956).
4. Dragonic, I., *Nucleonics*, **21**, 33 (Feb. 1963).
5. Rohm and Haas Bulletin, *Glacial Methacrylic Acid–Glacial Acrylic Acid*, August 1960.
6. Semenov, N. N., *Chemical Kinetics and Chain Reactions*, Oxford Univ. Press, London, 1935.
7. Chachaty, C., M. Magat, and L. Ter Minassian, *J. Polymer Sci.*, **48**, 139 (1960).
8. Magat, M., *J. Polymer Sci.*, **48**, 379 (1960).
9. McCurdy, K. G., and K. V. Laidler, *Can. J. Chem.*, **42**, 818 (1964).
10. Dainton, F. S., K. J. Ivin, and D. A. Walmsky, *Trans. Faraday Soc.*, **56**, 1784 (1960).
11. Morgan, P. W., *Mod. Packaging*, **22**, No. 1, 159 (1948).
12. Stannett, V., M. Szwarc, R. L. Bhargava, J. A. Meyer, A. W. Myers, and C. E. Rogers, *Permeability of Plastic Films and Coated Paper to Gases and Vapors*, Tappi Monograph Series, No. 23, Tappi, New York, 1962, (a) pp. 39-48; (b) p. 24.
13. Frisch, H. L., *J. Polymer Sci.*, **B1**, 581 (1963).

## Résumé

L'acide acrylique monomère placé entre deux films de polymères polymérise de façon quasi explosive à des doses de 0.3 Mrad en électrons. Il en résulte un lien entre les deux films et la préparation d'une couche interlaminaire d'acide polyacrylique. Des changements de perméabilité à l'oxygène sont dûs à la formation de ce sandwich. Le caractére

exothermique et le lien en résultant dépendent de la dose utilisée, de sa vitesse et du volume d'acide acrylique dans l'intercouche. Les résultats suivent qualitativement le mécanisme pour la polymérisation explosive discutée par Semenor et plus récemment par Chachaty, Magat, et Ter Minassian.

## Zusammenfassung

Zwischen zwei Monomerfilme gebrachte monomere Acrylsäure kann mit Elektronen bei einer Dosis von 0,3 Mrad zur fast explosiven Polymerisation gebracht werden. Die entwickelte Wärme führt zu einer Verbindung der beiden Filme und zur Bildung einer interlaminaren Polyacrylsäureschicht. Bei dem gebildeten Sandwich tritt eine Änderung der Sauerstoffpermeabilität auf. Die Wärmeentwicklung und die entstehnde Bindung sind von der Dosisleistung, der Dosis und dem für die interlaminare Schicht verwendeten Acrylsäurevolumen abhängig. Die Resultate stimmen qualitative mit dem von Semenov und neuerdings von Chachaty, Magat, und Ter Minassian für explosive Polymerisation diskutierten Mechanismus überein.