

Adhesion of Glow Discharge Polymers

ASHOK K. SHARMA,* FRANK MILLICH, and ECKHARD W. HELLMUTH, *Polymer Division, Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110*

Synopsis

Various reaction parameters in a propylene glow discharge polymerization were investigated with the objective of synthesizing films having good adhesion to metal and glass substrate. Monomer flow rate (at a constant pumping efficiency) was found to exert a significant effect on the quality of polymer adhesion to substrates. Good adhering polymeric films were obtained only at high flow rates where the deposition rate decreases with an increase in monomer flow rate. This observation applied also to ethylene, propane, allyl bromide, and ϵ -caprolactam. Transmission electron microscopy of the freshly deposited polymer films indicated a defect-free structure of the polymer surface obtained at high flow rates. The polymer surface obtained at low flow rates had a bead structure superimposed by uniformly placed circular defects.

INTRODUCTION

Polymeric deposits obtained through the glow discharge technique¹⁻⁷ find applications as corrosion-resistant coatings, reverse-osmosis membranes, biomedical membranes, encapsulation films, capacitor dielectrics, antireflection optical coatings, and light guides for integrated optics. In almost all these applications, the durability of coating is of prime importance; and one of the main factors that govern this durability is adhesion of the polymer to the substrate. In the past,⁸ we reported conditions for achieving an excellent adhesion of propylene synthesized in a tubular reactor to glass and aluminum substrates. The technique of improving hydrophilicity of plasma polymers by oxygen plasma etching was also referred. In the present study the principal of adhesion has been extended to other monomers. Transmission electron microscopy has been used to study the morphological features of the glow discharge polymer as a function of reaction parameters; especially the monomer flow rate, which produces a major change in adhesion of the polymer. A detailed investigation of oxygen plasma etching technique has been conducted both from a commercial and a theoretical point of view and are discussed separately.

EXPERIMENTAL

Polymer coatings were prepared in a tubular reactor (1 m long and 75 mm in diam) employing a flow-through mode of operation. A Tomac diathermy unit (model 1565), which operates at a radio frequency of 27.120 MHz and delivers power in the range 100-150 W,[†] was used as the power source. The coupling

* Present address: Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, MO 65401.

† Information provided by the supplier of the diathermy unit.

was inductive and perpendicular to the reactor. Micro glass slides (dn $60 \times 25 \times 1.02$ mm) cleansed with hydrofluoric acid, and an aluminum foil carefully wrapped over a glass slide were used as substrate for polymer deposition. Each of these substrates was further cleansed by argon plasma etching prior to polymer deposition in the reactor. The use of argon plasma to remove tightly bound adsorbed gases from the inside surface of PETRA (Positron-Electron-Tandem-Ringbeschleuniger-Anlage) Al-vacuum chambers has recently been demonstrated.⁹

The detailed methods of substrate cleaning and polymerization have been described elsewhere.¹⁰ In brief, the polymerization consisted of diffusing monomer gas (from a monomer mixing reservoir system) into the evacuated reactor at a desired pressure and initiating plasma by turning on the diathermy unit. The pressure drop in the monomer mixing system was used for computing the monomer flow rate. The rate of polymer deposition varies with the monomer flow rate, reactor pressure, RF power, substrate position, and the presence of a reactive (such as BrCCl_3) and nonreactive (argon) gas in the monomer feed. Great care was therefore exercised in assigning these factors. Monomer gases (cp grade) were purchased from Matheson Gas products and were used as received. Ar (cp grade) was obtained from Airco Inc. and BrCCl_3 (99%) from Aldrich Chemical Co., Inc.

Most previous attempts¹¹ of measuring adhesion have used the "Scotch tape" method first suggested by Strong in 1945.¹² The method is obviously only qualitative and gives no indication of the relative magnitude of the adhesive forces if adhesion of the film to substrate exceeds adhesion of the tape to the film. It was noticed that certain coatings which had an excellent rating by the Scotch tape test peeled off on standing in air or by placing in boiling water, suggesting poor adhesion.

Since no suitable method for measuring adhesion of glow discharge polymer coatings has been reported in the literature, a simple test of assessing the polymer adhesion was developed which consists of determining the time polymer coatings take to peel off (or lift from) the substrate surface in boiling distilled water. The results indicated that weakly adhering coatings were lost from the substrate surface in a few minutes, while strongly adhering coatings were not peeled even after boiling in H_2O for several hours. The latter coatings were also resistant to boiling saline solution or to organic solvents such as benzene at room temperature. Since the polymer coatings are quite hydrophobic (contact angle with H_2O 90°) compared to the base substrate (glass or metal) their presence or absence on a substrate surface could be easily ascertained by contact angle measurement.

Transmission electron micrographs of polymer surfaces were taken by the carbon replica technique using a Hitachi, model Hu 11E, electron microscope. Samples for electron microscopy were prepared by depositing polymer on a cleaned glass substrate placed at the center of the reactor RF coil where the highest deposition rate was observed. The deposition time varied from 15 to 45 min. Presence and supply of fresh monomer in the reactor beyond the plasma reaction was avoided by cutting off monomer flow a few seconds earlier than the RF power. This helped in investigating true features of plasma polymers and left no place for the growth of polymer by a conventional reaction mechanism. The pressure in the reactor was released against argon so as to avoid direct ex-

posure of the samples to air. Each polymer surface was then replicated almost immediately using the resin Pulver Schnellhartner (Technovit Corp.) in a Technovit solvent.¹³ Direct deposition of polymer on a 300-mesh grid was also attempted. For this purpose the grid was first coated with a film of parlodion (0.5% solution of parlodion in amyl acetate), followed by carbon evaporation, and deposition of polymer as described earlier. The grid was viewed directly in the electron microscope without any further treatment.

RESULTS

Adhesion

An investigation of the effect of polymerization parameters viz. monomer flow rate, polymerization time, substrate position, substrate material, presence of inert or a reactive gas during polymerization, and monomer type reveals that monomer flow rate has the maximum effect on the quality of polymer adhesion to a substrate. In general, the adhesion was improved by an increase in monomer flow rate (at constant pumping speed) and reached an excellent rating at high flow rates beyond the maximum in a monomer flow rate versus deposition rate curve (Fig. 1);⁸ before and at the maximum the adhesion was poor (0A–3A rating by Scotch tape test). An increase in deposition rate with monomer flow rate throughout the flow rates studied was observed when BrCCl_3 , a reactive gas, was mixed with the monomer¹⁰; addition of 5 mole% of BrCCl_3 to the feed mixture gave coatings with a temporary 5A rating of adhesion at much higher monomer flow rates, which started peeling on standing for six to seven days in air or by subjecting to a rapid boiling test. These observations lead to the conclusion that the best quality of adhesion is achieved only under conditions where the depo-

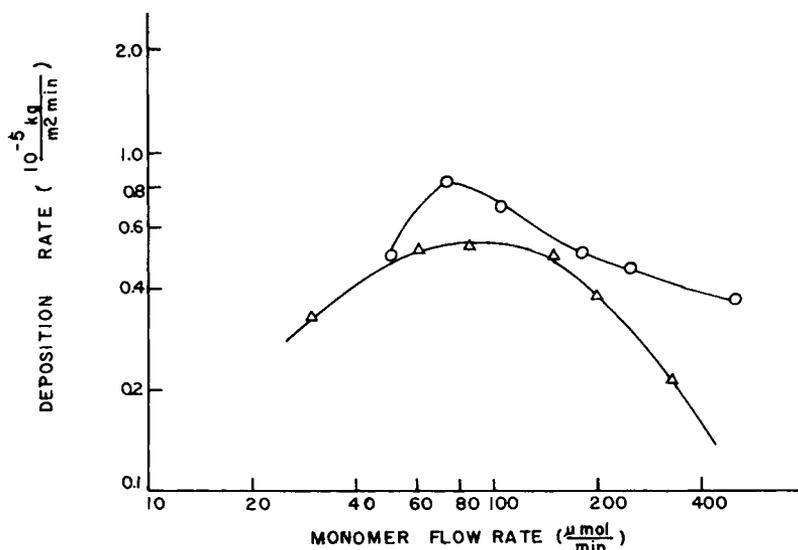


Fig. 1. Variation of glow discharge of polymerized propylene (Δ) and ethylene (O); deposition rates as function of monomer flow rate on logarithmic scales (polymerization time, 3 hr; substrate position, 140 mm from center of coil).

sition rate decreases with increase in monomer flow rate. This view was supported by the flow discharge polymerization of ethylene, propane, allyl bromide, and ϵ -caprolactam monomers. The first three of these were polymerized in a manner similar to propylene polymerization. However, considerable difficulty was encountered in introducing sufficient amount of monomer into the reactor during ϵ -caprolactam polymerization.¹⁴ The problem was finally overcome by keeping granular ϵ -caprolactam in a glass ampule directly in the reactor (near its inlet end). The flow rate of the monomer in the reactor was varied by changing the pumping speed of the system. Polymerizations were conducted at zero pumping speed (closed system), low pumping speed (mechanical pump only), and high pumping speed (with diffusion pump). An attempt to increase the monomer flow rate by flowing different concentrations of argon over the solid caprolactam was also made.

The results of ethylene polymerization were similar to propylene polymerization except that the maximum in the flow rate versus deposition rate curve was shifted to lower flow rate and SMC, the adhesion of the polymer to substrates (Fig. 1).¹⁵ (With propane, the deposition rate decreased with increased flow rate, and adhesion was good throughout the range studied.) Allyl bromide, which showed an increase in deposition rate for all the flow rates examined, had poor adhesion at all these flow rates.¹⁵ The ϵ -caprolactam behaved similarly. Here too, monomer flow rate exerted the maximum effect on the quality of polymer adhesion to substrates, but adhesion was not improved by incorporating argon with the monomer (beyond point C in Figure 2). None of the films, however, was resistant to boiling saline solution. The maximum resistance (15 min) was offered by films obtained at the highest pumping speed. Perhaps the poor adhesion of ϵ -caprolactam polymer is related to oblation of the polymer by atomic

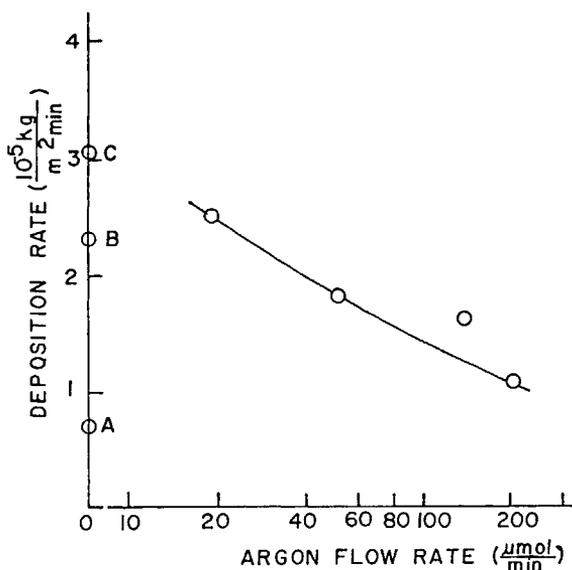


Fig. 2. Glow discharge polymerized ϵ -caprolactam deposition rate as function of system pumping speed and argon flow rate. (A) closed system; (B) pumping with mechanical pump; (C) pumping with diffusion and mechanical pumps, polymerization time, 90 min; substrate position at the center of RF coil.

oxygen produced in the flow discharge. Poor polymer adhesion in the presence of N_2 and/or Ar gas on polysilazane thin films was reported by Wrobel and Kryszewski.¹⁶

As reported earlier,⁸ polymerization time and substrate position affect polymer adhesion only at low monomer flow rates. The quality of adhesion is improved by reducing the deposition time or by placing the substrate away from the electrodes. Thicker films obtained by increasing polymerization time at low flow rates had a tendency to buckle and crack presumably due to stresses incorporated during deposition. Yasuda and Morosoff¹⁷ found that the intrinsic stress in glow discharge polymers is an expansive one and originates from the wedging of reactive species of plasma between the chain segments of the already formed polymers.

Polymerization conditions that provided good polymer adhesion to Al and glass substrate also gave good adhesion on tin and copper substrates. The rates of polymer deposition were comparable.

Morphology

It was of interest to study the morphology of glow discharge polymerized propylene as a function of monomer flow rate because this variable produced major changes in the adhesion of polymer-to-glass and metal substrates. Samples for transmission electron microscopy prepared by 'replication technique' proved quite satisfactory. No incorporation of plasma polymer in the replica, as reported by the earlier workers,^{18,19} was observed. The replica technique circumvents the deleterious effects of the electron beam on the polymer, which has been reported by Thompson,²⁰ for low energy (~ 25 keV) electron microscope beams. Direct deposition of the polymer film on a 300-mesh copper grid was unsuccessful. The glow discharge polymer film could not be grown in the grid holes and attempts to obtain a carbon support film on the grid in a vacuum evaporator failed. A carbon film transferred onto the grid from mica support was lost in the reactor during argon etching. A conventional method of obtaining support from a parlodian plastic film coated with carbon proved to be of some help but electron micrographs appeared murky, which could be due to the deformation of the plastic support film during plasma treatment.

Figure 3(A)–(E) show the electron micrographs of glow discharge polymerized propylene films obtained at different monomer flow rates viz. 45, 120, 220, 320, and 386 $\mu\text{mole min}^{-1}$. Figure 3(F) shows the TEM micrograph of a glow discharge polymerized ϵ -caprolactam surface. All of the micrographs except the one in Figure 3(F) (polymer obtained at highest flow rate) show nearly circular inhomogeneities (surface defects) of varying size at the polymer surface. The diameter of these circulooids (two dimensional equivalent of spheroid), 0.2–0.84 μm , varied with the polymerizing conditions. The size of the circulooids increased with increasing flow rate to a maximum size at about 120 $\mu\text{mole min}^{-1}$ (near the maximum in flow rate versus deposition rate curve). Higher flow rates resulted in circulooids of decreasing diameter. At the very high flow rate of 380 $\mu\text{mole min}^{-1}$ no such substrates were observed at the polymer surface. The surface concentration of circular inhomogeneities decreased with increasing flow rate. At 320 $\mu\text{mole min}^{-1}$ flow rate, the entire grid surface contained only six such structures and at 380 $\mu\text{mole min}^{-1}$, none were observable.

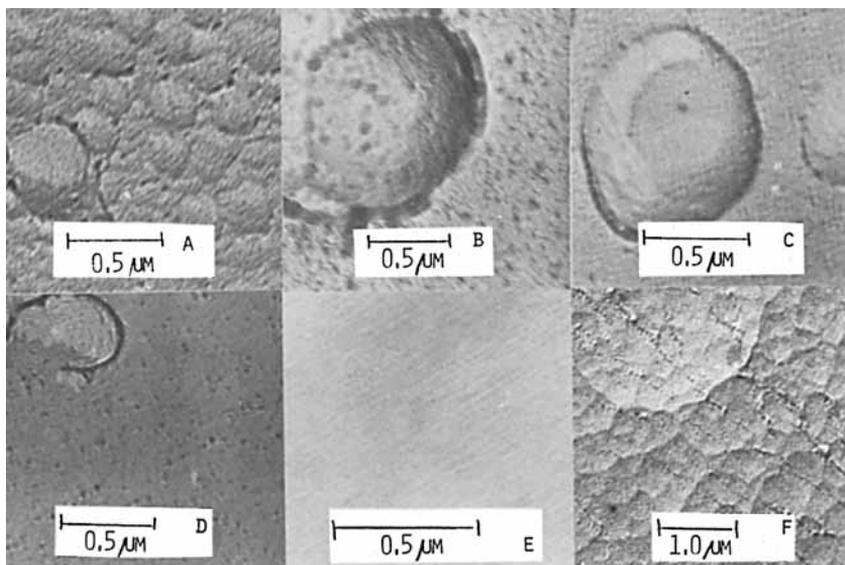


Fig. 3. Transmission electron micrograph of glow discharge polymerized propylene obtained at a monomer flow rate of (A) $45 \mu\text{mole min}^{-1}$ (38 250 \times); (B) $123 \mu\text{mole min}^{-1}$ (35 700 \times); (C) $225 \mu\text{mole min}^{-1}$ (44 200 \times); (D) $326 \mu\text{mole min}^{-1}$ (39 950 \times); (E) $386 \mu\text{mole min}^{-1}$ (60 350 \times); (F) transmission electron micrograph of glow discharge polymerized ϵ -caprolactam (16 060 \times).

The physical nature of the circulloids is not clear. No pronounced shadowing is observed in the electron micrographs, which suggests that they are not spherical. Also the diameter of the circulloids is sometimes two to three magnitudes larger than the calculated average thickness of the film. However, a careful examination of the micrograph of the polymer obtained at low flow rate [Fig. 3(A)] shows smaller spherical particles with 200–300 Å diam. These particles approximate the structure size indicated by Schmidt's small angle x-ray scattering studies of an ethylene glow discharge polymer.²¹ It is likely that several of the smaller spherical structures collapse together due to expansive stresses to form circular structures. Another interpretation of the circulloids may lie in the microlifting of the polymer film after deposition owing to poor adhesion. Whatever the case may be, the results of transmission electron microscopy are in accordance with the concept of adhesion developed in the previous section. The polymer films having good adhesion also had a relatively defect-free surface structure.

DISCUSSION

The vast difference in polymer adhesion at very low and very high monomer flow rates can be explained by postulating different sites of polymerization under two extreme conditions: a gas phase polymerization at low monomer flow rates and a predominately surface polymerization at high monomer flow rates. Similar views have been expressed by other workers.^{22–24} At low flow rates, smaller numbers of molecules are fed into the reactor and energy imparted per molecule from the electric field is quite high. This leads to extensive bond breaking in the molecules, and hence, an increased radical concentration in the gas phase.

Under such circumstances a gas phase polymerization prevails resulting in the formation of polymer beads as indicated by the transmission electron microscopy of the deposited polymer at low flow rates. The beads obtained at low flow rates are only physically placed on the substrate surface without any specific interaction. Additional polymerization at the substrate surface links the particles together but does not make them key into the surface. Mass spectral analyzes of gaseous effluents from the reactor further support gas phase polymer. Hydrocarbon products up to C_{12} were identified in the mass spectra of effluents at low monomer flow rate.¹⁵ Direct evidence of gas phase polymerization at low monomer flow rates is provided by the flow discharge polymerization of the ethylene monomer. The formation of needle-shaped particles along the cross section of the reactor was observed. Since there was an over supply of monomer in the reactor at high flow rates, the adsorption of the monomer at the substrate surface and the occurrence of a surface reaction was not surprising. The average energy imparted from the electric field to each monomer molecule under these conditions becomes lower than a threshold value due to an increase in the number of molecules and a decrease in electron acceleration path. This reduces collision efficiency and the polymerization rate declines. Glow under such conditions becomes very feeble and then completely disappears at very high flow rates. The growth of polymer at high monomer flow rates thus starts at the surface resulting in a mechanical interlocking of the polymer into the defect (microcavities) of substrate surface, and hence, provides better adhesion. Incorporation of $BrCCl_3$ in the monomer feed results in an increased rate of gas phase polymerization and gives poor adhesion.

This study indicates that good adhesion of almost any glow discharge polymer to substrate can be obtained by a careful control of reaction parameters, especially the monomer flow rate. However, it has been frequently noticed that glow discharge polymerization is system dependent, and the results obtained in one specific reactor geometry must be applied with due consideration of the relatively large number of parameters that govern glow discharge polymerization processes.

References

1. R. J. Joyce, H. E. Sterling, and J. H. Alexander, *Thin Solid Films*, **1**(6), 481(1968).
2. A. M. Mearns, *Thin Solid Films*, **3**(3), 201(1969).
3. K. G. Mayhan, M. E. Biolsi, and M. R. Mavens, *J. Vac. Sci. Technol.*, **3**(2), 575(1976).
4. *Techniques and Applications of Plasma Chemistry*, J. R. Hollahan and A. T. Bell, Eds., Wiley, New York, 1974.
5. *Chemical Reactions in Electric Discharges*, Am. Chem. Soc., Washington, DC, 1969.
6. H. Yasuda, in *Thin Film Processes*, J. L. Vossen and W. Kenn, Eds., Academic, New York, 1978.
7. *Plasma Polymerization*, M. Shen and A. T. Bell, Eds., Am. Chem. Soc. Symp. Ser 108, Am. Chem. Soc., Washington, DC, 1979.
8. A. K. Sharma, F. Millich, and E. W. Hellmuth, *J. Appl. Phys.*, **49**(10), 5055(1978).
9. A. Mathewson, J. Kouptsidis, and L. Hipp, in *Proceedings of the 7th International Vacuum Congress*, R. Dobrozomsky, F. Ruedenauer, and F. V. Vichboek, Eds., 1977, p. 235.
10. A. K. Sharma, F. Millich, and E. Hellmuth, in *Plasma Polymerization*, M. Shen and A. T. Bell, Eds., ACS Symp. Ser 108, Am. Chem. Soc., Washington, DC, 1979, p. 53.
11. S. Bateson, *Vacuum*, **2**, 365 (1952).
12. J. Strong, *Rev. Sci. Instr.*, **6**, 97 (1945).
13. R. F. Bills, *Electron Microscopy*, Western Publishing, Los Angeles, CA, 1974.

14. A. K. Sharma, F. Millich, and E. W. Hellmuth, *Polym. Prepr.*, Am. Chem. Soc. Div. Polym. Chem. **20**(2), 624 (1979).
15. A. K. Sharma, *An Investigation of Propylene Glow Discharge Polymerization*, Ph.D. thesis, Univ. of Missouri-Kansas City, MO, 1979.
16. A. M. Wrobel and M. Kryszewski, *J. Macromol. Sci. Chem.*, **12**(7), 1041(1978).
17. H. Yasuda and N. Morosoff, Preparation of Composite Reverse Osmosis Membranes by Plasma Polymerization, Office of Water Research and Technology, U.S. Contracts Nos. 14-30-3157 and 14-30-3301, 1979.
18. N. Niinomi, H. Kobayashi, A. T. Bell, and M. Shen, *J. Appl. Phys.*, **44**, 4317 (1974).
19. M. R. Havens, A Mechanistic and Structural Investigation of Plasma Polymerized Ethylene, Ph.D. thesis, University of Missouri-Rolla, MO., 1976.
20. L. F. Thompson, A Fundamental Investigation of the Gas Phase Polymerization of Styrene and Vinyl-Type Monomers in a Low Power Inductively Coupled 4 MHz RF Plasma, Ph.D. thesis, Univ. of Missouri-Rolla, MO, 1970.
21. M. R. Havens, K. G. Mayhan, W. J. James, and P. Schmidt, *J. Appl. Polym. Sci.*, **22**, 2793 (1978).
22. H. Carchano, *Commun.-Table Ronde Int. Trait, Surfa Polym. Plasma*, P. Fauchais, Ed., Univ. Limoges, France, 1977, RT12.
23. T. W. Scott, K. C. Chu, and M. Venugopalan, *J. Polym. Sci., Polym. Chem. Ed.*, **16**(12), 3213 (1978).
24. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **16**, 595 (1972).
25. G. K. Vinogradov, Yv. A. Avonov, and L. S. Polak, *Khim. Vys. Energ.*, **13**(1), 84(1979).

Received April 11, 1980

Accepted August 26, 1980

Corrected proofs received May 6, 1981