NOTE

Microwave Plasma Process for Gelatin Coating on Polyester and Cellulose Triacetate Film Bases

INTRODUCTION

Several works have demonstrated that plasma treatment can produce significant modifications in the surface layers of some materials. Particularly, it has been found that the adhesive bondability can be enhanced for polymers. Schonhorn and Hansen used a low-power radio frequency coil to modify the adhesive bonding of polymers.[1] At the same time, Goring performed experiments on the bonding strength of cellulose surfaces by submitting them to corona discharges.[2] Recently, Burkstrand deposited metal films on oxygen plasma-treated ABS polymer surfaces (acrylonitrile–butadienne–styrene).[3] All these surface changes were found to accompany an increase in the surface free energy, as reported by Owens.[4]

In the case of photographic film, emulsion layers are usually coated on a transparent polymer or cellulose base. However, in general, photographic emulsion layers do not adhere easily on the film base unless a special gelatin solution called "substratum" has been used for bonding.[5]

In our project, polyester and cellulose triacetate film bases were treated in a microwave plasma, and gelatin was coated directly to see whether the substratum operation could eventually be eliminated. We do not attempt to provide a technical comparison of actual photographic gelatins as these were not readily available. However, general commercial gelatins were used to demonstrate the feasibility of the process comparing the results of treated and untreated photographic film samples.

All of our experiments were performed in microwave plasmas generated by the LMP (large-volume microwave plasma) generator.[6] The LMP technique involves a cold plasma treatment.[7] We concentrated our attention on the action of different gases, time of treatment, and microwave power levels. The use of the LMP apparatus presents several attractive advantages: (a) more homogenous and larger-volume plasmas can be generated in the treatment reactor; (b) the absence of internal

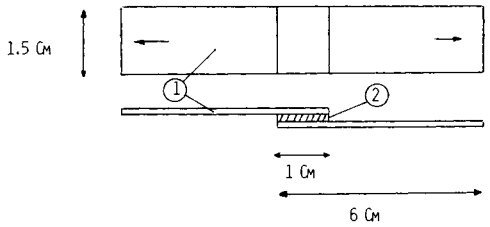

Fig. 1. Adhesion tests: 1, samples; 2, gelatin layer.

TABLE I
Relation Between Rupture Strength of Material and Length of the Overlap Zone (Oxygen-Treated Samples)

Materials	Sample	Rupture of material	Rupture of gelatin bond, kg: Length of overlap >2 cm	Rupture of gelatin bond, kg: Length of overlap = 1 cm
Polyester	1.5	28–30	>28–30	20–25
Cellulose triacetate	1.5	17–20	>17–20	10–15

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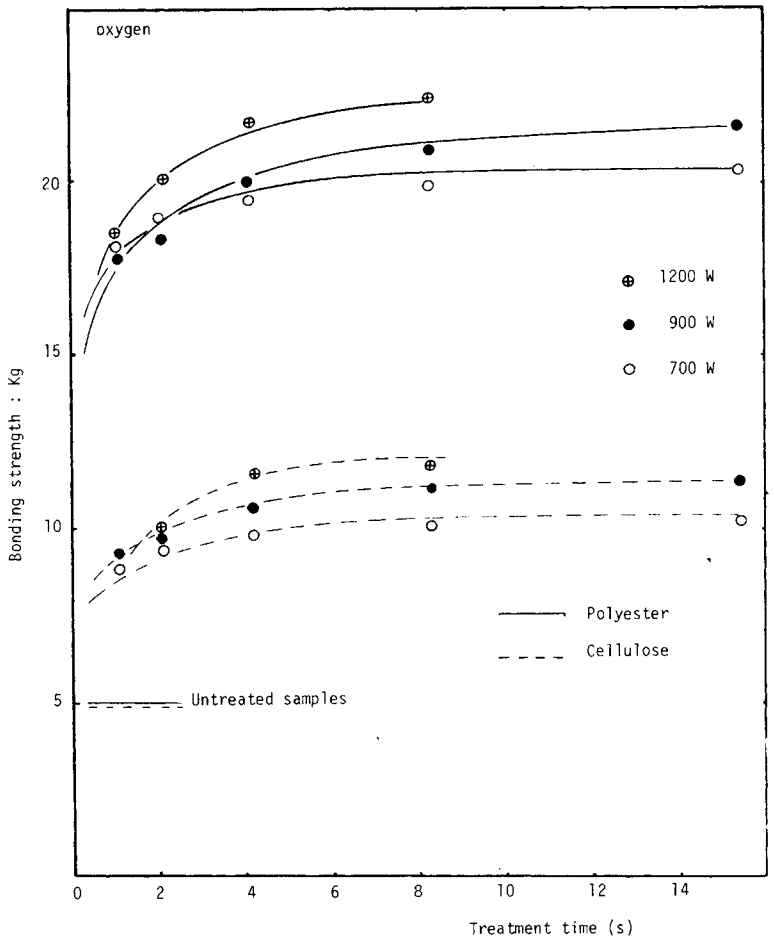

Fig. 2. Bonding strength versus treatment time in oxygen plasma (⊕), 1200 W; (●), 900 W; (—), polyester; (- - -) cellulose.

metallic electrodes prevent plasma contamination; (c) the carrier gas remains rather cool; (d) the absence of high voltage eliminates tedious experimental precautions; (e) the use of a slow-wave structure facilitates microwave matching.

EXPERIMENTAL

Different techniques of photographic gelatin coating have been reported in various reports and patents.[8–10] Thomas, Wheeler, and Miller used corona discharge for coating photographic emulsion layers.[11] The operating source characteristics were voltages of 25–50 kV, and frequencies 60 Hz to 10 kHz.

In the present report, it is useful to point out the main features of the LMP generator, although details have been reported in previous papers.[6] The reactor is a quartz tube which is placed above a planar slow-wave structure. The volume of the tube is approximately 6 cm^2 × 100 cm. The pressure of the gas is controlled at the inlet side of the tube by adjusting a needle valve, and this pressure is set at 1 torr by the use of a digital vacuum gauge. A vacuum pump at the opposite side of the reactor tube allows the pressure to be kept constant during the operation. The frequency of the microwave source is 2450 MHz, and the energy is transmitted by means of a WR 284 wave guide. A high-power dummy load is mounted at one end of the slow-wave structure to absorb any excess power not absorbed by the plasma.

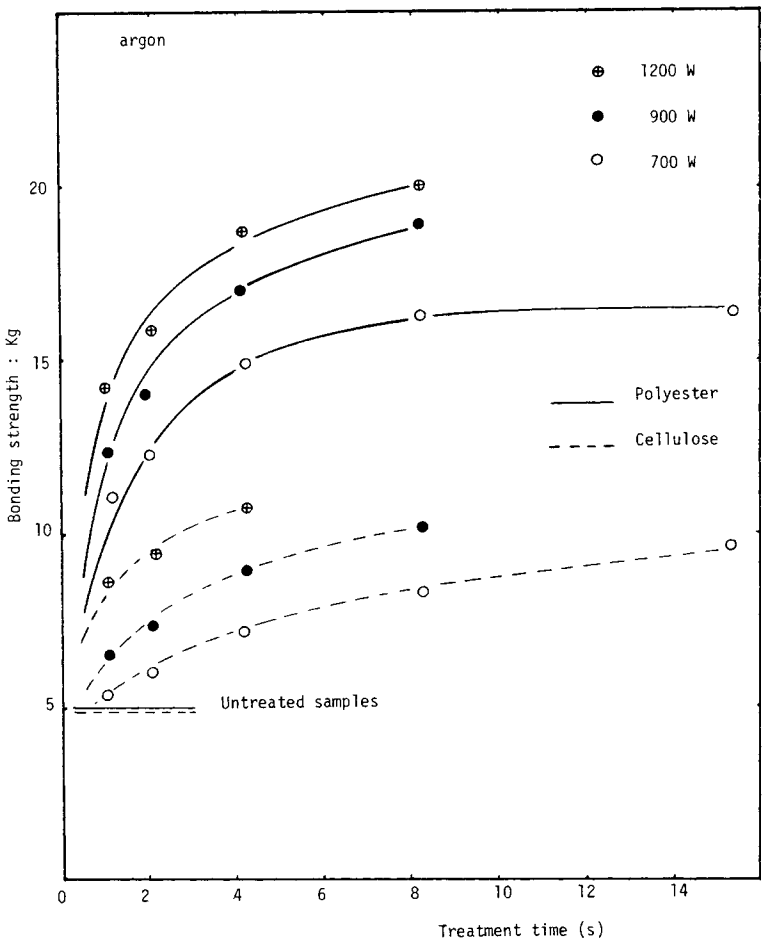

Fig. 3. Bonding strength versus treatment time in argon plasma (⊕), 1200 W; (●), 900 W; (ciop), 700 W; (—), polyester; (- - -), cellulose.

Polyester and cellulose triacetate sample strips were introduced into the reactor after a methanol and distilled water cleaning operation. The pressure was maintained lower than 1 torr for 15 min before opening the needle valve for any gas inlet. Then, pressure was set at 1 torr for another 15-min pumping period. The exposure time was varied from 1–20 sec depending on the microwave power level (700–1200 W) and the type of gas used. After treatment, the samples were immediately bonded to form the test specimens.

BONDING TESTS

Different polyester and cellulose triacetate films were used (Melinex 442 and cellulose triacetate 21T34 of ICI, Mylar 5 mil of du Pont, and Estar of Kodak).

A commercial gelatin was dissolved in water (1 g gelatin for 25 g water). The solution was heated to 90°C and coated on the freshly treated samples as illustrated in Figure 1. The temperature of gelatin solution should be maintained constant during the coating period to insure bonding uniformity. Samples were wet pressed under a load of 150 kg/m^2 during 24 hr and then air dried for another 24-hr period before being submitted to a shear-strength test similar to that of ASTM D1002-72. The thickness of the films was approximately 0.12 mm (5 mil). The bond strength of all treated strips

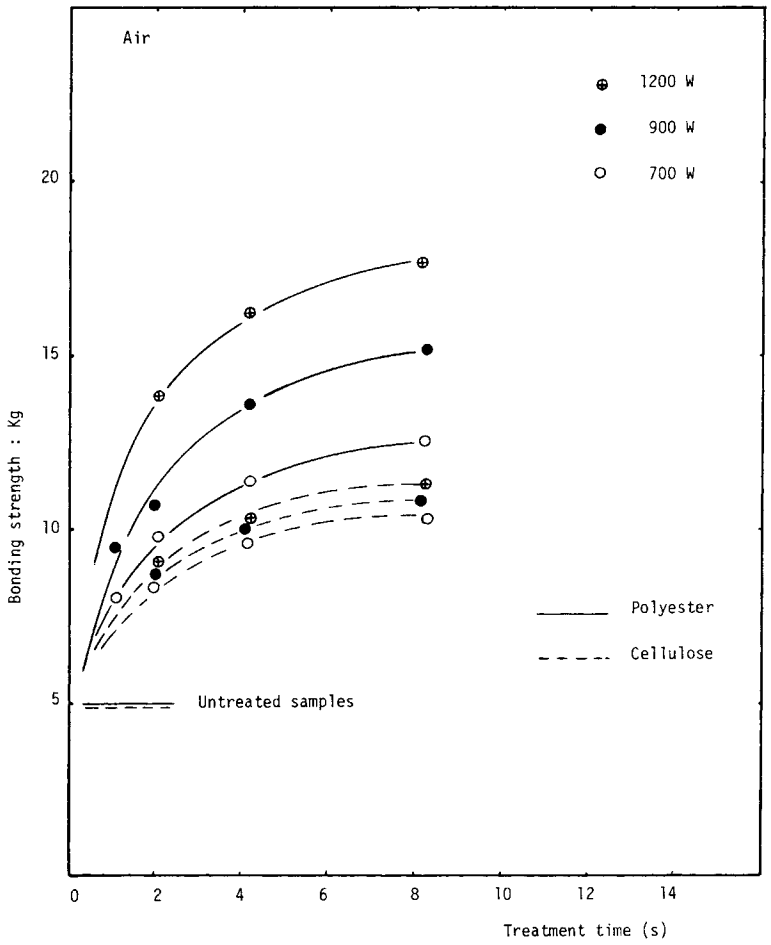

Fig. 4. Bonding strength versus treatment time in air plasma: For legend, see caption in Fig. 3.

should be tested below the yield point to avoid any plastic deformation during test.[12] The optimum dimensions of the overlapping zone were found to be 1.5 cm × 1 cm, and the corresponding value of rupture bond strength was 20–25 kg for the oxygen-treated polyester samples.

RESULTS AND DISCUSSION

The comparison between polyesters and celluloses corresponding to various experimental parameters is presented. Figures 2 and 3 plot the adhesive bond strength as a function of the treatment time in both oxygen and argon plasmas. The polyester samples show the most significant effects. Depending on the microwave power level and the treatment time, three- or fourfold increases in bond strength are observed (5 kg for the untreated samples). However, in Figures 4 and 5 we can see that the effects are less significant for both air and nitrogen plasmas under the same experimental conditions. In these figures some experimental data are not shown, since samples have been carbonized for certain conditions of power level and exposure time. Several attempts have been made to determine these optimum experimental conditions. The main parameter causing physical damages to the materials was only the temperature and not the microwave radiation. The Mylar polyester has a melting point around 250°C, and it is lower for the cellulose triacetate. Although oxygen is very active, a treatment time of 16 sec can be tolerated by the samples. In general, curves tend toward saturated values after 4 or 5 sec of exposure. The oxygen plasma showing the best bondability

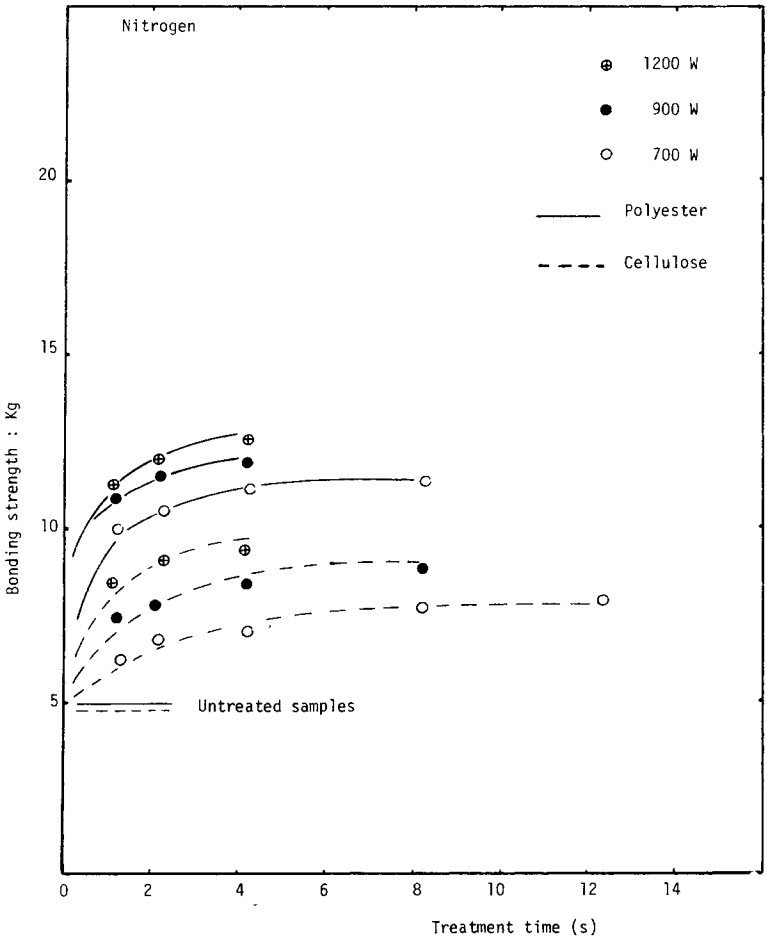

Fig. 5. Bonding strength versus treatment time in nitrogen plasma: For legend, see caption in Fig. 3.

concurs with the results outlined by Hall et al.[13] However, they had only a moderate improvement with the polyester film, whereas in this case the improvements are considerable.

No significant differences in the results have been noted with the various commercial marks of materials. Most of them gave satisfactory bondability conditions.

All the results shown in these figures were carried out with a 1.5 cm × 1 cm overlapping zone (Fig. 1). Other experimental work has been performed to find out these optimum dimensions. Table I shows some results for oxygen-treated samples. A 25–30-kg material rupture strength for a 1.5-cm-wide polyester strip can be seen; this requires an overlapping length of 1 cm corresponding to a bonding strength of 20–25 kg.

All of these plasma surface phenomena have been explained in the literature cited, and a detailed theory of adhesion has been exposed by Alner.[14] No attempt has been made yet to obtain other physical and chemical analysis of the treated samples.

CONCLUSIONS

Polyester and cellulose triacetate transparent films were treated in a LMP microwave plasma for photographic gelatin coating. Significant adhesive bondability improvements were observed with the oxygen, argon, air, and nitrogen plasmas. The use of the LMP slow-wave technique provided a convenient means of generating the microwave plasma and helped to eliminate electrode problems

in producing the corona discharge. An exposure time of 2–10 sec is sufficient to obtain three- to fourfold increases in the adhesion of gelatin coated directly into the treated film base.

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